#### A CHARACTERIZATION OF HAZARDOUS WASTE MATERIALS DISPOSED OF IN CALIFORNIA

FINAL REPORT

SUBMITTED TO:

STATE OF CALIFORNIA AIR RESOURCES BOARD SACRAMENTO, CALIFORNIA 95812

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This report was prepared by Science Applications, Inc. under the direction of the California Air Resources Board, however their oversight of the report does not signify the approval of the data developed in response to this technical direction.

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#### GLOSSARY

#### Class I Landfills -

Class I disposal sites are those at which complete protection is provided for all time for the quality of ground and surface waters from all wastes deposited therein and against hazard to public health and wildlife resources. The following cirteria must be met to qualify a site as Class I:

- (a) Geological conditions are naturally capable of preventing vertical hydraulic continuity between liquids and gases emanating from the waste in the site and usable surface or groundwaters.
- (b) Geological conditions are naturally capable of preventing lateral hydraulic continuity between liquids and gases emanating from wastes in the site and usable surface or groundwaters, or the disposal area has been modified to achieve such capability.
- (c) Underlying geological formations which contain rock fractures or fissures of questionable permeability must be permanently sealed to provide a competent barrier to the movement of liquids or gases from the disposal site to usable waters.
- (d) Inundation of disposal areas shall not occur until the site is closed in accordance with requirements of the regional board.
- (e) Disposal areas shall not be subject to washout.
- (f) Leachate and subsurface flow into the disposal area shall be contained within the site unless other disposition is made in accordance with requirements of the regional board.
- (g) Sites shall not be located over zones of active faulting or where other forms of geological change would impair the competence of natural features or artificial barriers which prevent continuity with usable waters.
- (h) Sites made suitable for use by man-made physical barriers shall not be located where improper operation or maintenance of such structures could permit the waste, leachate, or gases to contact usable ground or surface water.
- (i) Sites which comply with a, b, c, e, f, g, and h but would be subject to inundation by a tide or a flood of greater than 100-year frequency may be considered by the regional board as a limited Class I disposal site.

#### Class II Landfills -

Class II disposal sites are those at which protection is provided to water quality from Group 2 and Group 3 wastes. The types of physical features and the extent of protection of groundwater quality divides Class II sites into the two following categories:

Class II-1 sites are those overlying usable groundwater and geologic conditions are either naturally capable of preventing lateral and vertical hydraulic continuity between liquids and gases emanating from the waste in the site and usable surface or ground waters, or the disposal area has been modified to achieve such capability.

Class II-2 sites are those having vertical and lateral hydraulic continuity with usable ground-water but for which geological and hydraulic features such as soil type, artificial barriers, depth to groundwater, and other factors will assure protection of the quality of usable groundwater underneath or adjacent to the site.

The following criteria must be met to qualify a site as Class II:

- (a) Disposal areas shall be protected by natural or artificial features so as to assure protection from any washout and from inundation which could occur as a result of tides or floods having a predicted frequency of once in 100 years.
- (b) Surface drainage from tributary areas shall not contact Group II wastes in the site during disposal operations and for the active life of the site.
- (c) Gases and leachate emanating from waste in the site shall not unreasonably affect groundwater during the active life of the site.
- (d) Subsurface flow into the site and the depth at which water soluble materials are placed shall be controlled during construction and operation of the site to minimize leachate production and assure that the Group 2 waste material will be above the highest anticipated elevation of the capillary fringe of the groundwater. Discharge from the site shall be subject to waste discharge requirements.

Hazardous Waste - (California

Waste material or mixture of wastes which are toxic, corrosive, flammable, irritants, strong sensitizers or which generate pressure through decomposition, heat or other means which may cause substantial injury, serious illness, or harm to humans, wildlife, and the environment (California Administrative Code, Title 22, Division 4, Chapter 30, Section 66088).

Hazardous Waste - (EPA)

A waste is hazardous if it is a listed waste (40CFR 261,262) or if a waste is ignitable, corrosive, reactive or toxic as defined by the specific criteria of 261.21-261.24.

Kkg -

One thousand kilograms, equivalent to one metric ton.

mm Hg -

millimeters of mercury - a standard unit of measurement of pressure.

Toxic Air Contaminants - An air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health. Substances which have been identified as hazardous air pollutants pursuant to Section 7412 of Title 42 of the United States Code shall be identified by the state Board as toxic air contaminants.

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# SECTION 1 INTRODUCTION

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### INTRODUCTION

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#### INTRODUCTION

#### 1.1 BACKGROUND

Recent experiences in California and other states have shown that disposal practices for hazardous waste materials can impose serious risks to human health and to the environment. A lack of reliable data on the nature, source and quantity of the wastes has hampered assessment of impacts from such wastes. Further, the design of hazardous waste disposal sites has emphasized protection against contamination of both surface and underground water supplies, but air pollution problems associated with such disposal have not been widely considered. In recognition of these deficiencies in the assessment of air pollution from the dumping of hazardous materials, the California Air Resources Board (CARB) initiated a study to address these issues.

Science Applications, Inc. (SAI) has conducted a study for the CARB entitled "A Characterization of Hazardous Waste Materials in California", and this report presents the studies oriented toward its four major objectives:

- To conduct an inventory of hazardous waste sources in California and an identification of "volatile" portions of each source and the total;
- To evaluate the physical/chemical characteristics of hazardous wastes subject to on-site landfarming in California;
- To survey on-site hazardous waste incineration processes and practices in California as a combined source of airborne pollutants; and
- To evaluate a purge and trap test method for quantifying volatile organic compounds in waste streams.

The first three objectives, or tasks, are presented in the form of distinct chapters (2 through 4), which are related through the study's goal to increase

understanding of airborne pollutants related to hazardous/toxic waste disposal. The final study is prepared as a separate appendix to this report.

# 1.2 INVENTORY OF HAZARDOUS WASTES GENERATED IN CALIFORNIA (CHAPTER 2)

Existing data were evaluated in an attempt to determine the amount and type of hazardous waste generated in California. Performing this task involved a number of activities:

- existing data bases were evaluated relative to the volume and type of hazardous materials generated in the State;
- by using these data, a total volume of hazardous waste in the State was derived; then
- a comparative analysis was performed between the data bases generated by SAI and the University of California at Davis (UCD); and
- the volatile components in the State's hazardous waste inventory were identified and quantified; then
- methods were evaluated for determining the relative contribution to air contamination of on-site versus off-site treatment/ disposal.

The data used for this study were U.S. Environmental Protection Agency (EPA) Part A data bases, developed under the Resource Conservation and Recovery Act (RCRA) regulatory program whereby treators, disposers or storage facilities of hazardous waste must apply for interim status to continue to treat, store or dispose until a final permit is granted; California Department of Health Services (DOHS) studies; and other small scale hazardous waste inventories specific to California. In the evaluation of each data base, a description of its data content and an assessment of its applicability to this project have been included (Section 2.1). Also, in deriving a hazardous waste volume for the State, a determination was made of which data bases could best be used for this assessment, discussed in Section 2.2.

As a check of the accuracy of the hazardous waste volume estimate derived from these evaluations, a comparison was made with a previous, independent data assessment; this comparison is described in Section 2.3. Section 2.4 of this chapter presents SAI's determination of the volatile waste portion of the State hazardous waste inventory. The approach taken was to utilize EPA's Part A data base and RCRA waste codes to make a determination by Standard Industrial Classification (SIC) code as to the percentage of volatile material per industrial category.

In this portion of the study, a thorough, state-wide hazardous waste inventory was developed, although its precision and reliability is limited by the available data bases.

#### 1.3 CHARACTERIZATION OF LANDFARMED HAZARDOUS/TOXIC WASTES (CHAPTER 3)

Having evaluated the potential sources of air contamination from hazardous waste disposed in California, two direct investigations of treatment/disposal processes were undertaken to assess potential releases of contaminants to the atmosphere. Chapter 3 describes the first, in which petroleum refining landfarm processes were characterized for chemical constituents and potential for release to the environment.

Section 3.1 describes the types of industrial processes and landfarm wastes that were sampled. Also, a discussion is included to document the objectives in performing this aspect of the study, and to explain difficulties encountered in sampling and analysis.

The experimental methods used for this study are presented in Section 3.2. These methods include the field method sampling and analytical techniques for analyzing oil and grease, solids, moisture, heat of combustion, trace metals, base neutrals and compounds, pesticides, PCBs and volatile organics.

Section 3.3 reports the analytical results and discusses the potential emission of hazardous materials to the atmosphere from the landfarming operation.

#### 1.4 HAZARDOUS WASTE INCINERATION SURVEY (CHAPTER 4)

The data available on the California facilities which perform on-site incineration of potentially hazardous or toxic materials have been particularly scarce. For the second part of the direct investigation of California's waste handling practices, a survey of 19 hazardous waste incinerators was conducted. In contrast to the landfarm study, this was not an analytical effort but rather an overview of the destruction processes at each facility. This assessment of the incinerator industry included:

- an overview of the Federal, State and local regulations pertinent to the hazardous waste incinerators
- a discussion of the survey findings
- an evaluation of the potential emission to the atmosphere from hazardous waste incineration in the State.

The changing regulatory environment, as it relates to the incineration of hazardous waste, has resulted in the deactivation of some incinerators and an increase in regulatory control over other California incinerators. Section 4.1 summarizes the current regulatory status from the Federal, State and local perspective.

Of the 19 incinerator facilities, 11 owner/operators responded to SAI's request for data on their facility operation. The other seven facilities are either fume incinerators or have discontinued their incineration activities. Section 4.3 discusses the findings for those facilities and analyzes the status of incineration in California, relative to their potential for contributing hazardous air pollutants to the environment.

INVENTORY OF HAZARDOUS AND TOXIC WASTES GENERATED IN CALIFORNIA

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# INVENTORY OF HAZARDOUS AND TOXIC WASTES GENERATED IN CALIFORNIA

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# INVENTORY OF HAZARDOUS AND TOXIC WASTES GENERATED IN CALIFORNIA

The problems associated with the generation, treatment, storage, and disposal of hazardous wastes began receiving governmental and public attention in the late 1970's. The United States Environmental Protection Agency (U.S. EPA) promulgated the Resource Conservation and Recovery Act (RCRA) in 1976 in response to the growing need for tracking substances that were or could be considered threatening to the environment. The intent of RCRA was to provide the regulatory means for controlling the production, treatment, storage, and disposition of compounds recognized as hazardous waste.

The State of California, considered one of the forerunners in hazardous waste management, has attempted to assure compliance with RCRA and with additional State specified requirements. During 1982 and early 1983, significant advances were made in the State's ability to characterize hazardous waste and determine the quantities generated. The State agency responsible for regulating hazardous waste generation is the California Department of Health Services, Hazardous Waste Management Branch (CDOHDS/HWMB). This agency has been responsible for the maintenance of hazardous waste generation files. To achieve the objectives of their goals, the agency has developed a computerized data base for storing industry submitted manifest information.

While the California Department of Health Services has started to grapple with the issues of hazardous waste management in the State, other State agencies have sought to identify their regulatory responsibilities. Specifically, the California Air Resources Board (CARB) sought to inventory the hazardous waste generated in the State and then to identify the volatile components of that state-wide waste stream. CARB's interest in identifying the volatile constituents of the waste stream was to first assess the impact

of that volatile component to human health and environment and secondly to determine if the potential exists for regulating the volatiles as a means of mitigating these environmental hazards.

In attempts to meet the objectives of CARB, SAI proposed to quantify and characterize significant hazardous waste streams in the State. Characterization was intended to be performed by industry segment and according to the volatile properties of the waste stream. SAI was directed to perform the study using previously collected data, in doing so to evaluate all data bases which have analyzed any aspect of California hazardous waste generation issue.

The results of this task have been organized as subsections of this chapter, addressing each of the objectives. Section 2.1 describes the evaluation of the major sources of information on hazardous waste generation searched including: the U.S. EPA-RCRA Part A Application Permit data base; University of California at Davis data base; California Department of Health Services data base; California State Board of Equalization data base; TRW small volume generator study; Handbook of Industrial Waste Composition; California Department of Health Services Hazardous Waste Generation Report; Statewide Assessment of Hazardous Waste Management Facility Siting Requirements; Air Pollution Impacts of Hazardous Waste Incineration; A California Perspective; and County Surveys from Alameda, Ventura, and San Mateo. Section 2.2 provides estimates of the quantities of hazardous waste generated. Section 2.3 presents a comparison of the information and a validation of the major data Section 2.4 contains the results of the estimation of volatile wastes generated and Section 2.5 summarizes and gives conclusions of the findings of the task.

# 2.1 EVALUATION OF MAJOR SOURCES OF INFORMATION FOR HAZARDOUS WASTE GENERATION

The first objective in inventorying California hazardous weste, was to evaluate the information currently available for generation of hazardous wastes. Potential sources of information were identified. In addition to

Federal and State data bases, numerous studies have been conducted in an attempt to characterize and quantify hazardous waste generation in the State of California.

- The U.S. EPA RCRA Part A Application Permit data base
- University of California at Davis data base
- California Department of Health Services data base
- California Department of Health Services Hazardous Waste Generation Report
- Statewide Assessment of Hazardous Waste Management Facility
   Siting Requirements
- California State Board of Equalization data base
- Air Pollution Impacts of Hazardous Waste Incineration; A California Perspective
- TRW Small Volume Generator study
- Handbook of Industrial Waste Composition
- County Surveys from Alameda, Ventura, and San Mateo.

Each source of information utilized has been described in this section. The description of the source, its strengths and weaknesses, and the applicability of the data contained within each source relative to the development of accurate inventories are presented.

The existing sources were found to be informative in that they provided background data and an understanding of previous attempts to assess hazardous waste in the State.

The data bases were, however, limited in their ability to quantify and characterize in detail the California hazardous waste profile. SAI was able to utilize these data in attempts to quantify the waste stream and was further able to identify data gaps and potential future sources of data to

complete the waste characterizations. These issues are discussed in greater detail later in this section.

#### 2.1.1 U.S. EPA-RCRA Part A Application Permit Data Base

#### Data Base Description

The Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act gave the U.S. EPA authority to promulgate national standards for the location, design, operation, monitoring, closure, and post-closure care of facilities which treat, store, or dispose of hazardous waste (December 18, 1978). The intention of the standards was to protect human health and the environment by monitoring the design, construction and operation of hazardous waste management facilities in accordance with Section 3004 of RCRA.

By November of 1980, all facilities which treated, stored, or disposed of hazardous wastes were required to file a Part A Permit Application. Compliance with this request gained the facility an interim status authorizing continued operation until a Part B Permit Application was required by the EPA. To adequately handle the data generated from the Part A Permit Applications, each EPA regional office was responsible for processing the permits and entering the information into computerized data bases.

For the SAI study, EPA Region IX (located in San Francisco, California) was used as the source of Part A Permit Applications. EPA Region IX includes the States of California, Arizona, Nevada, and Hawaii. According to data available in May 1982, 914 Part A Permit Applications had been filed for Region IX. Of the 914 Applications, approximately 850 were submitted by California facilities, the rest were submitted by Arizona, Nevada and Hawaii. Only the Applications filed by the California facilities were used in this study.

The data requested in the Part A permit application included:

- Description and location of facility
- Standard Industrial Classification (SIC) codes applicable to the facility and a description of the business
- Description and estimates of the amount and type of treatment, storage, and/or disposal activities
- Description and estimates of the amount of hazardous waste generated
- An engineering schematic of the facility
- Copies of existing environmental permits.

In describing the type of waste generated by a facility, the RCRA waste codes were utilized. These waste codes identify wastes alphanumerically under the following categories:

- Non-Listed Toxic Waste on Notification (includes any combination of Arsenic, Barium, Cadmium, or Chromium wastes)
- Non-Listed Characteristics of Hazardous Wastes (includes ignitable, corrosive, and reactive wastes)
- Contaminants Characteristic of EP Toxicity. EP Toxicity is an elution procedure (hence EP) which is an analytical technique used in determining if a compound contains hazardous characteristics. This EPA developed test, includes an elution procedure followed by analysis for specific metals, pesticides and herbicides.
- Hazardous Wastes from Nonspecific Sources (includes sludges from gray iron founderies, still bottoms, paint residues, oil bath sludges, distillation side cuts, cleaning solvents, and wastes from nonspecific sources)
- Hazardous Wastes from Specific Sources (includes sludges, residues, bottoms, ends, tars, slop oils, blowdown solids, solvent cleaning wastes, and various wastes from specific sources)
- Chemicals Manufactured/Formulated for Commercial or Manufacturing Use (compounds identified by generic and trade names).

The waste codes relate to either specific chemical compounds, or to a particular industrial waste stream.

#### Data Base Strengths

The data base resulting from the Part A Permit Applications represents one of the most complete sources of hazardous waste treatment, storage, and disposal activities available. The information contained within the data base is useful for hazardous waste management and regulation of facilities treating, storing or disposing of hazardous wastes. Information was provided on the breakdown of waste components so that an identification of volatile components of the hazardous waste can be estimated.

#### Data Base Limitations

The information contained within the data base was not conducive to making estimates of the types and quantities of hazardous materials generated. Limitations of the data base as a useful tool for accurately characterizing and estimating hazardous waste materials are:

- Applicants filed information concerning both existing operations as well as expected future operations. The Application does not distinguish between present operations and future plans.
- The Application does not provide for periodic updates in operational changes in processing conditions. The data base represents relative facility conditions at the close of the calendar year 1980.
- Waste characterization information does not differentiate between broad and more specific descriptors of the RCRA waste code and there are no provisions for future refinement of generic waste code categories.
- Although the Application requested Standard Industrial Classification (SIC) Information, the SIC codes are not correlated to either the volume or type of waste generated by each process.

- Applicants may have inflated estimations of future operational conditions, which would result in elevated quantification of waste generation.
- The facility was not required to, nor were there directions for the selection of RCRA waste codes. The only instructions were to "Enter the code from the list of process codes below which best describes each process..."

These limitations are significant if the data base is to be used to accurately portray the characteristics of waste generated in California.

## Applicability

The Part A Permit Applications were useful for obtaining an overview of a facility's hazardous waste treatment, storage, and disposal practices. From the information provided in the data base, rough qualitative estimates of the characterization and quantities of hazardous wastes could be made, including the portion of the waste stream that was volatile. However, the limitations of the data base restricted the accuracy of the estimations for the following reasons:

- California regulates hazardous wastes more stringently including regulating small generators, and has a broader definition of what is a hazardous waste, thus the RCRA data base will not cover all hazardous waste generators in the State.
- The range of waste identification codes and their ambiguity impeded a detailed characterization of the hazardous wastes generated.

As will be discussed in detail later in this chapter, despite the limitations of this data base, the RCRA Part A file is currently the most comprehensive data file for evaluating California hazardous waste management practices. For this reason, the Part A data base was used in large part in SAI's analysis of the California hazardous waste inventory.

## 2.1.2 University of California at Davis Data Base

## Data Base Description

The University of California at Davis (UC-Davis) Department of Engineering, under contract to Governor Brown's Office of Appropriate Technology (UAT), conducted a study designed to determine the types and quantities of hazardous wastes generated by California facilities. UC-Davis created their own computerized data base using original Part A Permit Applications as the basis. Previously, UC-Davis had developed a hazardous waste code system similar to the RCRA waste code categories. (The conversions from RCRA to UCD waste codes used by UCD are shown in Appendix 2-1). As the first step in the analysis, UC-Davis assigned their waste code to each of the wastes reported in the Part A Permit Applications. The following correlations were performed on the resulting data:

- Estimations of total waste quantities generated
- Distribution of waste quantities by SIC code
- Distribution of waste quantities by UC-Davis waste code
- Correlation of the number of facilities reporting both SIC and UC-Davis waste codes.

Initially, UC-Davis performed these functions as the Part A Permit Applications were being submitted to EPA. The 1981 report generated by UC-Davis was representative of the partial data base. The second report issued in March, 1982 contained information on the completed data base. The data contained within both reports were reviewed by SAI.

#### Data Base Strengths

This study was useful in that it included a thorough engineering analysis of each of the Part A permits and was therefore able to perform a

more refined evaluation of the hazardous waste management status in California. Specifically, the analytical results of the distribution of waste streams by SIC Code and volumes is a unique data set amongst all the other California studies. Secondly, this study has considerable strength in the usefulness to the SAI study as a source of comparison of results and an indicator of the relative accuracy of the analysis.

## Data Base Limitations

Many of the correlations or analyses performed in the UC-Davis study were based on assignments made by an analyst. Quantities of wastes generated were assigned to SIC codes for facilities reporting more than one SIC code. However, the criteria used for assignment of the SIC codes were not clearly stated (i.e., whether additional information was obtained from the facility or additional information was acquired relative to the types of processing employed). The Part A Permit Applications provides descriptions of the facilities by numerous SIC codes, but does not categorize waste codes under specific SIC codes. While UCD has prepared a workable system of inventory, it is difficult to use in this study because many of the UCD analysis could not be replicated by SAI.

## <u>Applicability</u>

The UC-Davis study did provide a basis for comparison of the total quantities of hazardous wastes generated that were subjected to on-site treatment. The UCD study, while not particularly useful in expanding knowledge on hazardous waste inventories, was of benefit in looking at systems for assessing the relative risks of hazardous waste in the State. The use of this data is discussed in Section 3.0.

# 2.1.3 <u>California Department of Health Services Hazardous Waste Inventory</u> <u>Systems</u>

## Data Base Description

The California Department of Health Services, Hazardous Waste Management Branch (CDOHS/HWMB) has the responsibility for regulating and controlling hazardous waste generation within the State. When CDOHS was established in 1973, the Liquid Waste Haulers Manifest system was developed. The system was used for tracking the off-site disposal activities of both generators and haulers. The early manifest contained only 16 waste type categories. In 1977, a new manifest was introduced that included 76 waste categories. The manifest was modified further in October 1982 to accommodate additional information planned for inclusion in a computerized hazardous waste data base management system. Additionally, the HWMB reports to the State's Hazardous Waste Management Council. The HWMB has generated several studies and reports in response to this reporting structure. This section discusses the waste manifest system and the CDOHS reports.

#### Hazardous Waste Manifest System

Since 1973, CDOHS has maintained a hazardous waste manifest system. Preceeding RCRA by three years, it was developed to monitor hazardous waste disposal in the State. Under this system, liquid waste haulers were required to submit a manifest with summary information describing the origin and destination of their cargo, the volume/weight hauled and a categorical description of the contents.

Originally, the manifest system was maintained manually by CDOHS. Between 1973 and 1981, monthly reports estimating the magnitude of California's hazardous waste activities were generated. Because the demand for inventory information far exceeded the Department's capabilities, the Department recently (May, 1983) initiated a computerized data entry system.

The hazardous waste manifest system encompasses both off-site and on-site generation and transportation activities. Facilities that handle hazardous wastes are required to account for all wastes generated. In contrast to the Federal regulations, the State also requires small volume generators (<1,000 kg/month) to submit manifests.

The data collected by CDOHS includes information required by EPA's RCRA Part A Permit Applications such as process description, waste stream characterization, waste volumes, and disposal techniques.

Computerized entry of manifest data was initiated in October of 1982. When manifests are received, they are manually evaluated and entered into the computer. Of the 17,000 manifests that have been entered into the system, 50 to 60 percent have errors associated with incomplete or improper data entry by the generator. The manifests in error are placed in a "suspense" file until they are retrieved, corrected, and re-entered into the data base. From June 1981 until October of 1982, no manifests were processed for data base entry. A total of 33,000 manifests are planned for entry into the data base.

#### Data Base Strengths

The CDOHS data base contains valuable data for assessing the status of hazardous waste generation and disposal in California. The computerized information retrieval system will greatly augment the tracking and evaluation of hazardous waste in the State. Currently, trends in hazardous waste management can be determined, and it provides supportive data for conclusions drawn from other sources.

Once the data base system becomes totally functional, it will be one of the most informative sources for hazardous waste generation, treatment, storage, and disposal available for the State.

#### Data Base Limitations

The usefulness of the current system is limited for the following reasons:

- The computerized system has only been on-line since November of 1982; CDOHS is still improving and debugging the system
- The 18-month gap between the manual system and the computerized system resulted in data not being processed, therefore, information collected during that time period has not been considered in any inventory calculations.

These weaknesses are significant in that they limit the usefulness of the data base for analysis of California hazardous waste management practices.

## **Applicability**

The data base is incomplete, therefore a complete summary of hazardous waste generation in the State cannot be determined. The information obtained from this source does indicate trends in hazardous waste management. The available data was used in the SAI study to support the information available from other sources.

# 2.1.4 <u>California Department of Health Services Hazardous Waste Generation</u> Report

#### Data Base Description

The CDOHS prepared and submitted a report in August, 1982, entitled "Report to the Hazardous Waste Management Council on Current Hazardous Waste Generation in California." The report contained the department's estimation of the hazardous waste generated in the State. The Department based the approximations on data gathered from waste manifests, State Board of Equalization tax records, EPA Part A Permit Applications, national, State and regional studies, and county investigations. The report was presented in four parts:

- Off-site disposal facilities
- On-site disposal facilities
- Hazardous waste related activities
- Small volume generators (<1 000 kgs/month).</li>

#### Off-Site Disposal Facilities

CDOHS estimated the amount of hazardous waste disposed of at off-site facilities at approximately one million tons per year. This estimate was based on information contained in liquid waste haulers records in 1977 and 1978. Off-site wastes were categorized by waste code county and Class 1 landfill.

The CDOHS estimates were confirmed by the University of California Davis study (September 1981). This study concluded that the annual off-site disposal was 1.3 million tons in 1980. The more recent study using data collected between February and June of 1981 estimated 1.39 million tons of hazardous waste were handled off-site. When waste associated with site cleanups were included in the summary the estimated total increased to 1.5 million tons. Seasonal aspects of waste disposal clean up of hazardous wastes and other factors were included in the estimations.

#### Limitations of the CDOHS estimations were;

- Lack of truckload inspecton data for the inventory time period resulted in estimates based on producer's categorization of wastes;
- Age of data, and the resultant change in industry activity in the past economically disadvantaged years;
- Increase in contaminated soils from hazardous waste site cleanups;
- Recent reductions in the amount of waste shipped to off-site disposal as result of increased CDOHS fees;

- Recent CDOHS policy decisions on drilling muds and scrubber wastes; and
- Industry responses to financial responsibilities associated with RCRA.

The limitations of the data base are all attributable to the fact that the information contained in it is dated; this is especially critical in light of the severe changes in industrial process management in the past years.

## On-Site Disposal Facilities

The results of the CDOHS on-site disposal estimates indicated approximately 4 million tons of hazardous waste were generated per year. This estimate was based upon county surveys conducted from 1976 through 1978. The CDOHS report was compared with the UC-Davis study which estimated 4.8 million tons of hazardous wastes were disposed of on-site per year.

The limitations of the CDOHS estimate of 4.0 million tons of hazardous waste disposed on-site annually is that only 33 of the 853 RCRA Part A Permit Applications concerning on-site disposal were included in the estimate. Additionally, facilities using some forms of surface impoundments were not considered in the estimate.

A study conducted by Booze-Allen and Hamilton (1980) estimated the quantity of hazardous waste produced by EPA Region IX (Arizona, California, Hawaii, and Nevada) in 1980 was 2.8 million tons. Most of the waste originated in California. The estimate reflected on-site and off-site disposal, but did not include large volume waste producers of drilling muds, brines from oil, gas and geothermal exploration, or contaminated soils originating from spills and site cleanup projects.

Estimates of the on-site disposal of hazardous waste in California using the RCRA Part A Permit Applications (the DOHS study was performed by evaluating those disposers which had submitted Part A permits to EPA, DOHS also prepared county surveys based on the Permit data) are limited because:

- Lack of volume reduction information as waste materials passed through processing
- Over-estimation of waste generation quantities to avoid future limitations of business activities
- Double or multiple accounting of waste codes by facilities.

#### Hazardous Waste Related Activities

All wastes associated with on-site treatment, storage, and disposal as identified in the EPA Part A Permit Applications were included in this waste category. The category overlaps both the on-site and off-site disposal categories. The majority of the waste material identified was water or dilute aqueous waste treated and legally discharged into sewers and surface waters.

The CDOHS estimations for Hazardous Waste Related Activities were based primarily on the May 20, 1982 UC-Davis report (draft). The study included the review of 853 Part A Permit Applications. The number of permits included in the survey was 783. The CDOHS study estimated that 44 million tons of hazardous waste were generated annually in California. Of this 44 million, 4.7 million tons were estimated to have been disposed of on-site.

Rinse water/waste water represented over 60 percent of the total amount of hazardous waste in the State. Five other high water content categories accounted for over 33 percent of the total waste stream. The five categories were: corrosives; acidic solutions with heavy metals; other acidic solutions; aqueous solutions with heavy metals; and aqueous solutions with organic residues less than 10 percent.

In a later study (8/31/82), CDOHS, in a report to the Hazardous Waste Management Council, evaluated six months of manifest and other data and gave a refined estimate to the UCD data. This refined estimate also concluded that the amount of wastes attributed toward hazardous waste related activities was in excess of 44 million tons.

#### Small Volume Waste Generators

This category was included to represent generation and disposal practices. Small volume generators do not represent a significant contribution to the State's total waste generation. They are considered important because they are less likely to comply with local, State, and Federal hazardous waste regulations.

The CDOHS report, based upon an EPA funded study (TRW), states that 90.2 percent of the hazardous waste generators in the U.S. produced less than 1,000 kilograms/month of hazardous waste. Small volume generators accounted for 1.0 percent of the total hazardous waste generated. Generators producing less than 100 kilograms/month accounted for 74 percent of the total number of generators and 0.23 percent of the total quantity of waste produced. The report concluded that small volume generators (less than 1,000 kg/month) produced between 15,000 and 75,000 tons of hazardous waste per year.

The Office of Technology Assessment has challenged the EPA/TRW study. The Office informed congressional subcommittees that as high as 10 percent of the total waste generated may originate from small volume generators. The CDOHS report concluded that the 1 to 5 percent estimate of California's waste was within the range of the Federal estimations, therefore the findings were reasonable.

The relative hazards of wastes produced by small volume generators are important. The types of businesses that are encompassed in this classification are: printing firms; electronic component manufacturers, metal finishers; dry cleaners; fabricated metal producers; paint manufacturers; auto body shops; and agricultural chemical applicators. Typical wastes produced are: solvents, cyanide liquids, strong acids, and heavy metal compounds.

#### Data Base Strengths

The major strength of the study is that it is comprehensive in scope and made attempts to completely characterize hazardous waste generated in the State. Similar to the SAI/CARB study, it has reviewed and utilized to the extent possible previous studies performed in the State.

## Data Base Limitations

Use of existing sources was comprehensive. CDOHS in developing this study did not perform any additional analyses, but rather reported the data as it stood in the existing reports.

## Applicability

This study was useful in the overall SAI effort, in that it identified the data bases thought to be relevant to developing a State hazardous waste profile. It also pointed out the flaws of these data bases and the need for SAI to develop an analytical scheme in its attempts to inventory hazardous waste in California.

## 2.1.5 California State Board of Equalization 1981 Hazardous Waste Summaries

#### Data Base Description

The California State Board of Equalization maintains annual records on hazardous waste generated within the State. These records are based on excise tax imposed on hazardous waste generators, treaters, disposers and transporters operating in the State. A manifest system is required by generators for tax collection. Due to California confidentially laws, the State can only provide total tonnage per category. The record is divided into four categories:

- The amount of hazardous or extremely hazardous wastes which are not currently regulated by the Resource Conservation and Recovery Act. Consequently, this category covers two specific type of waste handlers: those handling less than 1,000 kg of hazardous waste per year, and those handling waste determined to be hazardous by the State but not by the Federal government.
- All waste which is not in the first category, but is classified as hazardous in California.
- All waste not identified in the above categories, but classified as extremely hazardous by the State.
- Waste from the extraction, beneficiation and processing of ores and minerals.

The 1982 report indicated that 1,241,072 metric tons of waste were from the 1st (RCRA exempt) waste category.  $^{1}$ 

## Data Base Strengths

The data base is extremely valuable as an indicator of the volume of wastes not regulated by RCRA, but of concern to California regulators. It provides an annual tally of the amount of waste handled in each of the respective categories.

#### Data Base Limitations

The raw data which served as input to this data base is considered to be confidential, as such, the State will only make available the volume numbers upon which the tax is levied. These volumes are not cross-referenced by any useful indicia such as site, location, type of waste, etc. Furthermore, because this waste tax is levied against generators, transportors, disposal and treatment facilities, the potential exists whereby the tax could be levied

<sup>&</sup>lt;sup>1</sup>This number was calculated by SAI based on the tabulation of the 1982 Board of Equalization Report.

multiple times when a waste is generated, transported offsite and disposed. This type of potential "double accounting" make it difficult to attribute the 1.2 million tons of hazardous waste solely to RCRA exempt generators, with any accuracy.

## Applicability

The Board of Equalization data base is valuable for identifying the volume of non-EPA regulated hazardous waste as defined by California. This data base is applicable to the CARB project for determining the volume of hazardous waste which cannot be determined using the Part A data base. The lack of information on production processes and waste characteristics limits the use of the data base for other than determining quantities of hazardous waste.

## 2.1.6 TRW - Small Volume Generator Study

## Data Base Description

In 1977, under contract to EPA, TRW conducted a study to determine the National volume of hazardous waste generated by small volume generators. This data base was developed to provide background data material support to EPA in preparing their hazardous waste regulations. At that time, small volume generators were defined as generating less than 5,000 kg of waste per year. This is in contrast to the current definition of a small generator which is less than 1,000 kg of hazardous waste per month. TRW surveyed 10 states and extropolated the data obtained from these states to a national estimate of waste volume. What TRW then reported was a summary document discussing this national waste volume. The raw data that was obtained from surveying the 10 states were considered confidential and were not published.

## Data Base Strengths

This study served as one of the first state or national surveys of hazardous waste generators. TRW introduced a novel approach for conducting a survey of this magnitude. It portrayed hazardous waste management practices in 1977, and is therefore useful as a comparison tool in analyzing trends in hazardous waste management.

## Data Base Limitations

The definition of 5,000 kg/year as a cutoff for small volume generators omits many generators from the current definition. Furthermore, in 1977 the definition of what was a hazardous waste is significantly different than what it is today. TRW's study is further weakened by its inability to report raw data, which would have enabled SAI to perform a refined analysis on the data for the CARB study.

The data base is not useful in this study because of the manner in which the study was performed and the change in the Federal regulatory posture on hazardous waste between 1983 and 1977.

#### Applicability

The value of the TRW study comes from evaluating how an updated study of larger magnitude could be conducted. Because of the dated nature of this report and the lack of access to the original data (in which individual facilities were identified) this report does not support our efforts.

# 2.1.7 California Department of Health Services (DUHS) - Handbook of Industrial Waste Composition in California

## Data Base Descriptions

In 1978, a study was conducted by DOHS of California hazardous waste streams to determine their chemical composition. The generic analysis was

performed by characterizing the waste stream associated with predominant 4 digit SIC codes. The data was gathered in meetings held with industrial representatives and by preparing an engineering evaluation of industrial processes to assess waste stream characteristics.

#### Data Base Strengths

The handbook provides a good overview and description of industrial waste streams; it is unique in the formatting of these characteristics by SIC code. The descriptions are accurate and useful for estimating the types of inorganic and organic constituents in the waste stream.

#### Data Base Limitations

The data base can not provide any information other than the generic descriptions; not all SIC codes are covered in this analysis. Occasionally the waste descriptions are too general to be particularly useful, this is especially true of process streams considered proprietary by industry.

## <u>Applicability</u>

The handbook is helpful for identifying volatile components of the hazardous waste stream. This study represents the best synopsis of waste stream characterization available, although it presents no total generation volumes and uses various units of measurement to express typical truck load size. Additionally the handbook is limited to waste streams that are taken off-site for disposal. Those industry categories which typically dispose of waste on-site are not considered in this effort.

## 2.1.8 California County Hazardous Waste Surveys

## Data Base Description

In 1972, EPA sponsored a study whereby California was to inventory their hazardous waste generators and disposers on a county by county basis. After three counties had completed their survey, EPA funding was stopped and the remaining counties in the State did not complete their study. The following summarizes the results of the three county survey:

- San Mateo County Study, prepared by the County Department of Public Health and Welfare. The study does not include the original data collected in the survey, rather reports volume of hazardous waste generated in the county.
- Alameda County Study is also a summary report with no data included on the individual dischargers.
- Ventura County Study was conducted in the same manner as the Alameda survey. By making a series of assumptions, small volume generator waste volumes could be calculated.

These surveys, unfortunately, only cover a small percentage of the total county surveys in the State and these counties do not represent the more industrialized counties in the State.

### Data Base Strengths

The county surveys were amongst the first to be performed by the State and represent an early attempt to quantify the hazardous waste generated in the State. Unlike other surveys, these studies were beneficial for showing generation patterns on a localized scale.

#### Data Base Limitations.

The weaknesses of these surveys are that not all the counties were surveyed and that the surveys were performed so long ago that the patterns of

hazardous waste generation have dramatically changed. Furthermore the definition of hazardous waste in 1972 is significantly different than it is today, and thus the assumptions used in this analysis can not be used for making current estimates.

#### Applicability

These surveys are useful in evaluating general waste generation patterns in the State. The volume estimates made in the survey cannot be used for their absolute value, but can be used to compare the amount generated between the counties.

## 2.1.9 Statewide Assessment of Hazardous Waste Management Facility Siting Requirements

#### Database Description

In September of 1983 the California DOHS prepared a report to the Hazardous Waste Managment Council on the availability of hazardous waste management facilities in the State. The objectives of the report were to predict the type and sizes of facilities which will be needed in the future in California. To develop this assessment, CDOHS reviewed the State's hazardous waste managements system the EPA Part A permit application the UCD database, and data from waste management facilities.

Using these data sources, the CDOHS revised its previous estimates of the amount of hazardous waste generated in the State. In this revised estimate, CDOHS omitted the UCD category 511 "Rinse Water and Wash Water"; the result was an estimate of 10 million tons per year, of which 87% of the wastes are managed on site. Estimates of generation were made on a regional basis around the State these estimates were used to make predictions on the regional needs for waste disposal facilities.

## Database Strengths

One of the major strengths of this study was that DOHS attempted to monitor waste handling facilities and generators to verify the accuracy of existing databases such as Part A and UCD. The information from generators was part of a five month study conducted in 1981 and focused on generators which had waste off-site. As a planning tool for State regulators and hazardous waste managers, this study is unique and highly valuable for the future. In particular the fact that the study was (conducted) on a Regional basis shows impressive foresight and planning. This DOHS study was also beneficial in that the waste streams which were included in the study were divided into gross categories for the purposes of identyfying different waste management options.

#### Database Limitations

By omitting the Rinse and Wash Waste category, the study overlooks a large quantity of waste which is generated on site. While this was necessary for accessing hazardous waste disposal needs, it severely limits the use of this study as a hazardous waste inventory database.

## **Applicability**

This study had little direct applicability to the SAI study, it was interesting that the study was initiated with the UCD and EPA Part A databases as its premises. Of particular interest was the conclusion that 87% of hazardous waste generated in the state is managed on-site. By this study's lack of accounting for the Rinse and Wash Water, little comparison of waste volume can be made to the SAI or UCD study. Also no conclusions were drawn concerning the databases that were studied and the field verification of generators.

## 2.1.10 Air Pollution Impacts of Hazardous Waste Incineration: A California Perspective

## Database Description

This December 1983 study is a report to the California Legislature prepared by the California Air Resources Board-Stationary Source Divison to investigate the role of incineration in California hazardous waste management. The results of an inventory of incinerated hazardous waste showed 48,000 tons/year of liquid organic hazardous waste and 191,000 tons of hazardous acidic wastes are incinerated on-site in the State. Available incineration techniques for hazardous waste were evaluated as well as the types and levels of emissions and the associated health impacts of specific pollutants. An assessment was also made of air pollution control devices that are available to mitigate these emissions, the regulatory (Federal and State) guidelines for hazardous waste incineration and an economic evalution of incineration versus other waste management alternatives.

## Database Strengths

The most obvious strength of this report is its comprehensiveness on the subject of California incineration, and putting the issue in perspective to National concerns. This study also provided a good summary of the technology, control technologies and the regulations surrounding incineration. Although vast quantities of reports have been published on these topics, the conciseness of this study is beneficial.

#### Database Limitations

As an overview of hazardous waste incineration in Califonia, this study has very few weaknesses. It would have been helpful to have more detail on the specific facilities (generators) which are incinerating waste, but doubtlessly the proprietary nature of the processes limited that evaluation.

## <u>Applicability</u>

This study has little applicability to the SAI effort, but provided a good source for understanding some of the specific technical issues of incineration. SAI was not able to use this source to compare with its own inventory of on-site California incinerators.

## 2.1.11 Summary of Data Base Evaluations

SAI evaluated the existing data bases and surveys that were applicable to inventorying hazardous waste in California. There are considerably more data sources available in California than for other States, but there is relatively little data available for a thorough inventory and characterization of hazardous waste. The data sources have mostly been surveys that were performed before the recent changes in hazardous waste definitions and regulations.

In performing the detailed evaluation of the data bases, SAI concluded that attempts to characterize the State hazardous waste streams would not be possible on a detailed basis without conducting its own surveys. Rather, SAI concluded that it could estimate the volume of hazardous waste generated in the State and the percentage of that volume which was considered volatile.

In the following sections, SAI describes the methods used to determine the volume of hazardous waste generated in the State, the technique used to estimate the accuracy of the volume calculation and the method used to determine the volatile component of the waste stream.

#### 2.2 DERIVING HAZARDOUS WASTE GENERATION QUANTITIES

An initial program objective was to attempt a determination of how much and what type of hazardous waste was being generated in California. The

inventory was to be based on all waste which was considered hazardous and regulated by California. The available data sources to be used for this estimate have been presented in the previous section. Major emphasis was placed on data originating from RCRA Part A permit applications and the small volume generator data from the State Board of Equalization. Table 2-1 shows the estimates of waste volumes made in prior studies.

TABLE 2-1. WASTE GENERATION SUMMARIES FROM VARIOUS DATA BASES.

	Dispo	sal Practices <sup>f</sup>		
Reference Page/Citation	Off-Site (metric tons)	On-Site (metric tons)	Total (metric tons)	Reference
CARB/9/UCD	1,358,562	44,350,341	45,708,903	1
OAT/15/22 <sup>a</sup> /UCD	1,358,562		5 X 10 <sup>6</sup>	2
OAT/20 <sup>a</sup> /UCD	1,359,883		<del></del>	2
CDOHS/7-8 <sup>b</sup> /UCD	1,539,892			3
CDOHS/7-8/27 <sup>C</sup> /CDOHS 8/82 stu	1,394,032 dy	44,542,551	45,936,583	3
CDOHS/19 <sup>d</sup> /UCD		4,753,956		3
Board of Equal <sup>e</sup> / 1981 tax			3,481,160	4
Board of Equal <sup>e</sup> / 1982 tax			2,494,896	4
So. Cal/UCD	1,358,562	43,421,715	44,780,277	5

<sup>1</sup>An Assessment of the Volatile and Toxic Organic Emissions from Hazardous Waste Disposal in California, California Air Resources Board (CARB) 2/11/1982

<sup>2</sup>Alternative to Land Disposal of Hazardous Waste, An Assessment for California, Office of Appropriate Technology (OAT) 1981

<sup>3</sup>California Department of Health Services (CDOHS) - Current Hazardous Waste Generation in California

<sup>4</sup>California State Board of Equalization - Personal communication

<sup>5</sup>Southern California Hazardous Waste Management Project, Hazardous Waste Generation and Facility Development Needs in Southern California

<sup>&</sup>lt;sup>a</sup>Same report, different totals

b Includes contaminated soil

<sup>&</sup>lt;sup>C</sup>Does not include contaminated soil

d<sub>On-site</sub> storage

eTaxed only, mainly off-site

f Many references evaluate waste generation by the disposal practices used for the waste material

An overall estimate was made for the annual volume of hazardous waste generated in the State; this number, however, should be used cautiously within the confines of how the data were developed. The following describes the process that SAI followed in obtaining a hazardous waste generation volume for California.

## 2.2.1 Inventory Methods

Data from generators which produce greater than 1,000 kg/month (from the RCRA Part A Permit Applications and UC-Davis data bases) were used to estimate the volume of hazardous waste (as defined by RCRA) generated in the State. The basic assumption in using these data is that most generators practice treatment, storage, or disposal of their hazardous waste and thereby are included in the Part A data base; that is, those who reported that they treat, store, or dispose of waste are likely to also generate that waste. One exception to this are the treatment and disposal industries which handle the waste from other generators only. These permittees are listed under SIC Code 4953 and 4212, and were not included in this analysis since attempts to include them would erroneously inflate the volume of waste generated in the State.

Some hazardous waste generators do not store their wastes for more than 90 days and are, therefore, exempt from filing a Part A application under RCRA. However, such facilities were considered to be uncommon and to usually be only small-volume generators.

Due to the lack of any other data source, therefore, SAI used the Part A permit applications to derive a State-wide generation volume. Each computerized Part A application was evaluated by SAI; in doing so the individual facility was compared with the waste codes and volume of waste reported in the application. Those permittees listed as SIC code 4953 and 4212 were not evaluated. SAI then tabulated the waste volumes reported by each applicant as their total waste volume. In doing so, an attempt was made to discount any obvious double accounting or erroneous entry of data. Using the

assumption that the remaining permittees are also generators,  $\underline{40,453,000}$  metric tons of hazardous waste were determined to be generated annually in California by facilities subject to EPA regulations. In Section 2.3 of this chapter, a discussion is presented of how this waste volume number compares with a similar study conducted by the University of California Davis (UC-Davis).

Recognizing that the Part A permittees do not include either the small hazardous waste generators (<1,000 kg/month) nor generators of waste subject only to the regulations by the State of California, SAI utilized the State Equalization Board data from its 1981 tax records. The taxes levied on hazardous waste are placed on generators, transporters and treatment, storage, The total amount of hazardous waste reported by and disposal facilities. small generators and non-EPA regulated waste streams is 1,241,100 metric tons per year. This estimate must be subject to careful review, since it may contain double accounting. Theoretically, both a generator, who turns his waste over to a transporter (who in turns transfers it to disposer), and the transporter could each be taxed for that same waste. Consequently, when looking at this estimate, a higher than accurate volume may be reported. However, when viewed in perspective, the quantities of waste contributed by these small generators represent such a small percentage of the total waste generated in the State, that there is probably little net effect on the inventory from such "double accounting" problems.

## 2.2.2 Inventory Results

SAI's technique for estimating the volume of hazardous waste generated in the State relied on two major data bases - RCRA Part A data base and the State Board of Equalization tax base. Using a set of assumptions, SAI tabulated the volume of waste generated annually in the State. This number, while it is felt to be relatively accurate, is limited by the incompleteness of the individual data bases and the accuracy of the data reported by the individual permittees.

To further check the accuracy of SAI's quantification effort, a detailed comparison of this study was made with that performed by the University of California - Davis. Both studies used the Part A data base, but under different sets of assumptions and considerations. The results of this comparison to determine accuracy are reported in the following section.

## 2.3 COMPARISON OF UC-DAVIS AND EPA RCRA PART A PERMIT APPLICATION DATA BASES

One of the major efforts of the inventory task was to compare the data base obtained in this study with the UC-Davis waste characterization study. UC-Davis performed two efforts in their analysis, each time using the original Part A permit applications. As discussed in Section 2.1, UC-Davis correlated codes using waste volumes and number of facilities to SIC and RCRA waste codes.

In a July, 1982 discussion with Dr. Ollis of UC-Davis, the last part of the study had been concluded and it was indicated that UC-Davis estimated 44,500,000 metric tons of waste treated, stored or disposed by on-site facilities in the State. As in the method used by SAI (discussed in Section 2.2), UC-Davis excluded transporters and commercial disposers from their analysis and used a similar tabulation methodology in deriving their estimate. UCD also excluded facilities which reported SIC 4953 and 4212 as their industrial identifier; they also tabulated their data by individual facility and used only one waste volume reported for each application. Analytically, the 9.1% variation between the volume of waste generated estimate made by SAI and that made by UCD is an acceptable discrepancy and reveals that the results are highly comparable. However, there are differences:

• UC-Davis used data from 783 Part A permits collected in November of 1981 and March of 1982. SAI used Part A data developed in April of 1982. Changes in regulations, and a re-evaluation of permittees, could contribute to a different profile of the permittees.

• UC-Davis used the original Part A applications and performed their own conversion of reported units to metric tons assuming one density for all wastes. SAI used EPA's waste values which are potentially different than the conversion factors used by UC-Davis, since SAI could not verify the method employed by UCD.

UC-Davis performed several other correlations that could not be reproduced or replicated in this study. Specifically, UC-Davis assigned their own waste codes to RCRA waste codes. Often, the UC-Davis waste codes were general and did not represent a one-to-one correlation to a specific waste type. The UCD list showing the correlation of UCD to RCRA waste codes is given in Appendix 2-1. A second correlation was performed by UC-Davis between SIC codes and waste volumes. Section 2.1 addresses the inadequacies of the Part A data for attributing waste volume to SIC codes. To overcome this, UC-Davis assigned percentages of the waste streams to reported SIC codes based on UC-Davis knowledge of the individual facilities operation. Again, this type of analysis could not be duplicated by SAI. Although not in complete agreement with the UC-Davis study, SAI considers the study helpful in understanding hazardous waste management practices in the State, particularly where on-site and offsite disposal practices and categorization of waste stream data are needed.

From the analysis of the UC-Davis and SAI studies, approximately 42 million metric tons of hazardous waste are generated annually in California. The comparison of the two studies indicates that this waste volume number is reasonably accurate, given the reliability of the Part A data base. Attempts to verify the accuracy of this number further were not possible due to the weaknesses of the other data bases.

## 2.4 ESTIMATION OF VOLATILE HAZARDOUS WASTE GENERATION

Having estimated the volume of waste generated in California, to the best extent possible, SAI then estimated the type and volume of volatile waste generated in the State. The estimations of volatile waste were performed in two parts; determine the volatility of specific wastes, and estimate the total portion of the California waste stream which is volatile.

## 2.4.1 Volatility Estimates by Waste Code

CARB requested SAI to determine the volatility of 38 specific UC-Davis codes and supplement the list with wastes containing metals in non-volatile form. They were:

001	216	248	287
004	217	250	288
006	· 221	254	289
007	222	255	446
009	223	261	447
211	224	263	454
212	225	281	457
213	227	282	523
214	241	284	
215	245	285	

Table 2-2 is the result of this effort, which shows the RCRA code, the comparable UC-Davis code, volatility and other properties. A close inspection of the Table reveals that not all of the UC-Davis codes have identified compounds with associated volatility. These specifically are:

001	214	263	288
004	215	281	446
006	217	282	523
007	245	284	
009	254	285	
212			

These UC-Davis codes are not always specifically defined and do not have specific compounds which characterize the waste stream and which would facilitate development of a volatility calculation for the waste code. Examples of the non-specificity are:

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES

UCD Code	RCRA Code	Constituents	Calculated Vapor (4) Pressure (1) (mmHg)	Vapor (4) 1) (mmHg)	Literature Vapor (1) Pressure (mmHg)	Solubility (1) in water (mg/1)	% Composition (2,3)	Toxicity (5)
211	U032	calcium chromate carbolic acid (Phenol) tetrachloromethane	ND 0.34 114.2	0.63	0.75 ( ) 93.1 (20 <sup>0</sup> C)	82,000	28	C
223	K031	by-product salts generated in production of MSMA and cacodylic acid						
227	P009	Ammonium picrate ND phenyl mercury acetate ND Nickel carbonyl 7-oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid (Aquathol) 2-sec-Butyl-4,6-dinitrophenol (Aretit)	ND ND ND e-2,3-dicarbo	40 bxylic aci	00 (25,8°C) d (Aquathol) ND ND			
255	(K044,K045)	Wastewater treatment sludges from manufacture of explosives, Spent carbon from wastewater treatment containing explosives	s ves, r ives,					
261	U238	Urethane Chloroethene 1,1-Dicloroethylene	ND 2,660.1 4,	4,101,3 633,8		v SS 1		GT, C GT, C
289	K048	DAF float from refining industry (petroleum),						
454	F017, F018 K078-K082	Paint residues, wastewater treatment sludge from industrial painting. Solvent cleaning waste, water cleaning wastes, wastewater treatment sludge from paint manufacturing.	treatment ing. er cleaning t sludge					

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES (continued)

UCD Code	RCRA Code	Constituents	Calcula Pressu	Calculated Vapor Pressure (1)	Literature Vapor Pressure (1)	Solubility (1) in water (mg/1)	% Composition (2,3)	Toxicity
213	F001	tetrachloroethylene methylene chloride trichloroethylene 1,1.1-trichloroethane carbon tetrachloride chlorinated fluorocarbons	18.5 355.5 74.3 ND 114.2	18.0 430.5 72.9 11.3 98.9	19 350(20°C) 77 100(20°C) 93.1(20°C)	150 20,000 1,000(20°C) 950 800	17(2) 12 9 12 9 12 28 (22)	) X 0 0 0
2-35	F002	tetrachloroethylene methylene chloride trichloroethylene 1,1,1-trichloroethane chlorobenzene 1,1,2-trichloro-1,2,2- trifluoroethane 1,2-dichlorobenzene trichlorofluoromethane	18.5 355.5 74.3 ND 12.0 334.1	18.0 430.5 72.9 121.3 11.8 292.8 1.5	$10(22^{0}_{C})$ $270(20^{0}_{C})$ $1,6$ $687(20^{0}_{C})$	488 10 145 1,100	13(2) 13 17 6 6 3 1	. 15 15
216	F003	xylene(s) (o-xy acetone ethyl acetate ethyl benzene ethyl ether n-butanol cyclohexane	(o-xylene) 6,6 229,9 96,8 9,5 9,5 534,2 6,2	6.6 201.3 82.7 9.8 463.6 7.8	6.0 ( )	175( )	18 <sup>2</sup> 3 2 2 2 2 2 1 1 1 1	
216	F004	cresols (m. (cresylic acid) (p. nitrobenzene	(ortho) 0,23 (meta) 0,18 (para) 0,09	0.44 0.18 0.16 0.23	0.04(20°C-meta) 0.11(25°C-para) 1.0(44°C)	23,500(20°C-meta) 24,000(40°C-para) 1,900	<1(2) <1 < 1	T sc
216	F005	methanol toluene methyl ethyl ketone methyl isobutyl ketone carbon disulfide isobutanol pyridine	126.9 28.4 94.7 19.9 360.9 10.4	121.0 26.9 97.0 7.2 337.8 12.7 18.9	100(21°C) 28.4 100 16(20°C) 260(20°C) 10 20	miscible 470 1,000,000 19,000 2,200 95,000(18°C)	11(2) 11 7 3 3 3 41	10

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES (continued)

RCRA Code	Constituents	Calculated Vapor Pressure (1) (mmllg)	Literature Vapor Pressure (1)	Solubility (1) in water (mg/1))	% Composition	Toxicity
	alkali metal Cn salts alkaline earth CN salts (Na, K, Ca) heavy metal CN cpds ferro-, ferricyanides ferric ammonium ferrocyanide	1,5×10 <sup>-20</sup> (NaCN)				
1	pentachlorophenol tetrachlorophenol benzene toluene benzo(a)anthracene benzo(a)pyrene chrysene naphthalene fluoranthene phenol 2,4,6-trichlorophenol 4,6-dimethylphenol 2,4-dimethylphenol	ND 7.6×10 <sup>-4</sup> ND 95.2 73.0 28.4 26.9 ND N	1( ) 1( ) 0.75( ) 1( ) 1( ) 1( )	1(14) 100 1(0,011) 1(0,012) 1(30) 82,000 1(0,28) 800 16,000		C
K002-K008	Pb CR ferric ferrocyanide (ferrocyanide→ HCN+)	Sludge	106(IICN)			
коо9, ко 10	chloroform formaldehyde acetaldehyde (product) methylene chloride methyl chloride paraldehyde . formic acid chloroacetaldehyde	194.7 173.1 3,840 4,454.5 900.6 928.1 355.5 4,311 4,045 ND ND 42.8 288.4 ND	140( ) 740( ) 350(20°C) 25,3(20°C)	8,000 3,800 120,000		SC, M, T  M  M  CT  CT  M  CT  CT

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES (continued)

Toxicity		sc T, 2, 2 (GT)	н, 2 GT По	(17, C, T (17, C (17, C, T (17, C (17, C	ст, с, (м) ст, с, (м) с ст
% Composition	<pre>&lt;0.05(K011) &lt;0.05(K011) &lt;0.001(K013)  0.7(K011)  0.32(K013)  0.30(K013) </pre>				2 (3) GT (T) (T) (T) (T) (T) (T) (T) (T) (T) (T
Solubility <sup>(1)</sup> in water	73,500 2,155,000 400,000 Miscible	2,200 800 6,000,000(0°C)	488	I I 800	SS SS
Literature Vapor Pressure (1) (mmllg)	85.5( ) 1.6( ) 223( ) 106 70.5( )	160(20°) 91(20°) 8bCl <sub>3</sub>	10(22°C)	22(100 <sup>0</sup> ) 63( )	12.5
calculated Vapor (1)	107.4 ND 277.4 ND 88.9	173,1 98,1 (ND) 24,299 8,124 147,895	1.3 11.8 26.9 0.28	2.6 × 10 <sup>3</sup> ND 98.9 0.72	15.7 1.1-) 30.2 1,2,3-) 3.0 0.9(1,3-)
Calcula Pressu	105.8 ND 271.3 ND 86.3	194.7 114.2 114.2 (ND) ND 7501.5	ND 12.0 28.4 ND	ND ND 114.2 ND ND	ND  ND (1,1, 3,33(1,2
Constituents	acrylonitrile(products) acrylamide acrolein HCN acetonitrile	carbon tetrachloride Sb cpds.(antimony chloride) chlorotrifluoromethane (products) chlorodifluoromethane tetrafluoromethane	benzyl chloride(product) chlorobenzene toluene benzotrichloride	hexachlorobenzene hexachlorobutadiene carbon tetrachloride hexachloroethane perchloroethylene	epichlorohydrin(product) chloroethers bis(chloromethyl)ether bis(2-chloroethyl)ethers trichloropropane dichloropropanols
RCRA Code	K011-K014	K021 (products)	K015	K016 (product)	к017
UCD Code	K011-225 K012 > 224 K013 > 224 K014-224	₹ 2-37	222	222	222

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES (continued)

UCD Code	RCRA Code	Constituents	Calculated Vapor (1) (mmllg)	g )	Literature Vapor Pressure <sup>(1)</sup> (mmHg)	Solubility (1) in water (mg/1)	% Composition (2,3)	Toxicity
222	K018	ethyl chloride(product) l,2-dichloroethane trichloroethylene hexachlorobutadiene	1,173.8 1,08 7 7 7 ND N	1,086.1 76.2 72.9 ND 2.6 x 10 <sup>3</sup>	1000(20°C)	1 SS SS SS	32 6 32 6 43 6	GT, C, M GT, SC, (H) GT, C, T GT
2 <b>-</b> 38	K019	ethylene dichloride(product) 1,1,1-trichloroethane 1,1,2-trichloroethane 1,1,1,2-tetrachloroethane 1,1,2,2-tetrachloroethane trichloroethylene tetrachloroethylene carbon tetrachloride chloroform vinyl chloride	79.0  ND 24.1  ND ND 14.3 18.5 114.2 194.7 12,660.1 4,10 ND	76.2 121.3 23.2 13.3 6.4 72.9 18.0 98.9 173.1 4,101,3	16.7(20°C) 19.19 93.1(20°) 140 ( )	\$\$ 1 1 8\$ \$\$ 1 (800) 8000 8000	3 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	GT, C, M, T GT, C, M, T GT, C, M GT, C, M GT, C, SC GT, C, ST GT, C, ST GT, C, T GT, C, T
222	К028	l,1,1-trichloroethane(product)ND vinyl chloride 4,1	01,3 4,	121,3 4,101,3		1 88	5 5	GT, SC, М GT, C
222	K029	1,2-dichloroethane 1,1,1-trichloroethane(product)ND vinyl chloride vinylidene chloride ND chloroform	9.0 50.1 34.7	76.2 121.3 4,101.3 633.8 173.1	140 ( )	SS 1 8S 1 1 8000	G1 G	GT,C,M,T GT,C,M,T GT,C GT,C GT,C
525	KO30 products	hexachlorobenzene hexachlorobutadiene hexachloroethane 1,1,1,2-tetrachloroethane 1,1,2,2-tetrachloroethane trichloroethylene perchloroethylene	ND 2.6 ND ND ND ND ND 1 ND ND 1 74.3 7	2.6 x 10 <sup>-3</sup> ND 0.72 13.3 6.4 72.9 18.0	22(100°C)	1 SS SS SS SS	15 61 61 61 61	GT, C, T GT, C, T GT, C, M GT, C, M GT, SC GT, SC

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES (continued)

UCD Code	RCRA Code	Constituents	Calculated Vapor Pressure (1) (mmlg)	Literature Vapor (1) Pressure	Solubility (1) in water (mg/l)	% Composition (2,3) T	Toxicity
K023-224 K024-248 K093>7 K094	KO23, KO24 KO93, KO94	phthalic anhydride (product) maleic anhydride naphthoquinones quinones PNA's(tars)	0.31 0.02 0.31 0.39 ND ND ND ND ND	<0.075( )	6200( ) SS-S SS	TS D D S S	
248	K025	1,3-dinitrobenzene 2,4-dinitrotoluene nitrobenzene(product)	ND N		SS(3000) SS(2000) SS	T9	
2 22	KO26 (product	paraldehyde pyridine picolines (product) methyl ethyl pyridine	ND ND 20.7 18.9 5.7 10.3 ND ND	10 22 10	miscible miscible miscible SS	75 <sup>(3)</sup> GT,SC 8	
224	K027	toluene diisocyanate(product) ND toluene diamines ND tar polymars (e.g., benzidimidazapore) ferric chloride	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-3 ~0.01(20°)		3 (3) SC 60 (SC)	
222	K032-K034 K097	chlordane(product) hexachlorocyclopentadiene heptachlor other chlorinated organic	ON O	1 × 10 <sup>-5</sup> 3 × 10 <sup>-4</sup>	I(0,009) I(25) I(0,05)	or, sc cr cr cr	
241	K036, K037	disulfoton(product)  toluene 0,0,0-triethyl ester of Phosphorodithioc acid	ND ND 28,4 26,9 ND ND	28.4			

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES (continued)

ncp · code	RCRA Code	Constituents	Calculated Vapor Pressure (1) (mmHg)	Vapor ) (mmHg)	Literature Vapor Pressure (1)	Solubility (1) in water (mg/l)	% Composition	Toxicity
241	K038-K040	phorate(product) formaldehyde phosphorodithioic acid phosphorodithioic acid esters	ND 3,839.6 ND	ND 4,454,5 ND		(05)1	75 H, 3 TP	
K048-259 K049-287 K050-431 K051-286 K052-447	K048-K052	Pb Cr					0-0,005(K048) 0-0,006(K051) 0-0,003(K048) '0-0,11 (K051)	
251	K053-K059	PB Cr (sulfides, sulfates acidic +H <sub>2</sub> S)	8)					
431	K061	Cr Pb Cd						
ė.	K095	1,1,2-trichloroethane(product) 1,1,1,2-tetrachloroethane 1,1,2,2-tetrachloroethane	t) 24,1 ND ND	23.2 13.3 6.4	16,7(20°)	1 88 88	(GT,	GT, SG, M GT, G, M GT
· ·	K096	1,2-dichloroethane 79.0 1,1,1-trichloroethane(product)ND 1,1,2-trichloroethane 24.1		76.2 121.3 23.2	16,7(20°)	88 1 1	GT, GT, GT,	GT, C, M GT, SC, M GT, SC, M, T

TABLE 2-2. VOLATILITY PARAMETERS OF HAZARDOUS WASTES (continued)

Toxicity		ema)
% Composition (2,3)		n for non-mammalian syst
Solubility (1) (mg/1)		SM - suspected mutagen M - listed mutagen ((M) - mutagen for non-mammalian systems) ST - suspected teratogen T - listed teratogen
Literature Vapor Pressure (n)		
Calculated Vapor Pressure (1) (mmHg)	e, nds,	T absent in source). s in stream/total mass of st
Constituents	Wastewater treatment sludge generated in production of creosote; wastewater treat- ment sludges from manufacture, formulation and loading of lead-based initiating compounds,	1 - values for 25°C unless specified ( ( ) indication of T absent in source). 2 - values based upon total annual U.S. consumption (mass in stream/total mass of stream) 3 - values based upon typical waste stream composition 4 - Reid RC, et al. The Properties of Gases and Liquids
RCRA Code	K035, K046	1 - values for 25°C unless specified ( 2 - values based upon total annual U.S. 3 - values based upon typical waste str. 4 - Reid RC, et al. The Properties of Gases
UCD Code	2 <b>-4</b> 1	1 - values 1 2 - values b 3 - values b 4 - Reid RC,

I - insoluble in  $\mathrm{H}_2\mathrm{O}$ SS - slightly soluble

GT - generally toxic

5 - Sax - Dangerous Properties of Industrial Materials

SC - suspected carcinogen ND - no data available

C - listed carcinogen

UC-Davis Code	<u>Definition</u>
212	Halogenated with other metals
214	Non-halogenated with heavy metals
215	Non-halogented with other metals
217	Unspecified solvents (probably volatile)

SAI used all the UCD and RCRA waste codes that were feasible for the purpose of developing volatility estimates. In addition other RCRA codes that do not compare with the UCD codes were added to the list and their associated volatilities were calculated.

The methods used for deriving volatility were:

I. Antoine Vapor Pressure Correlation - When a pure liquid achieves a state of equilibrium (equal chemical potential) between the vapor and liquid phases, the relation between the vapor pressure and temperature is expressed by the Clausius-Clapeyron equation:

$$\frac{d\ln P_{vp}}{d(\frac{1}{T})} = \frac{\Delta H_{vap}}{R}$$
 (Eq. 1)

 $P_{VD} \equiv vapor pressure (mm Hg)$ 

T = Temperature (°K)

 $\Delta H \equiv Enthal py of vaporization (Joules/mole)$ 

R ≡ Gas constant J oK mole

Antoine's Vapor Pressure Equation is a commonly used correlation based on the Clausius-Clapeyron equation. The constants for the Antoine equation are tabulated in standard physical chemistry references (Reid et al.). The integration assumes a certain dependence of Hvap/R on temperature, where Hvap = enthalpy of vaporization. In the integration, a constant is obtained which must be evaluated for a given vapor pressure-temperature point. Both Hvap and

Zvap are weakly dependent on temperature and pressure except near the critical point above which there is no coexistence (or differentiation) for liquid and vapor. This approach to estimating vapor pressures then seems valid for the range of ambient pressures and temperatures to be encountered for volatile organic waste disposal scenarios. Two methods for calculating vapor pressure, the Clausius-Clapeyron equation and the Antoine Correlation, were used to demonstrate the range of conditions which impact volatility measurement. The experimental conditions which are used to quantitatively measure volatility are different and will yield the range of vapor pressures (i.e., the two calculated values) shown in Table 2-2.

### 2.4.2 Estimating Volatile Portion of California Hazardous Waste Industry

Using the Part A Permit Applications data base, SAI attempted to calculate the percentage of volatile constituents in the hazardous waste streams of the State. The Part A data base lists the waste streams of each facility according to the RCRA code and volume reported by each facility for that stream. The volatility calculations in the previous section provided an estimate of the volatility of specific compounds contained in certain waste These estimates were used to estimate the relative volatility of waste streams according to RCRA and UCD waste codes. This judgement of volatility was made using multiple sources which describe the properties of each coded waste stream. SAI then calculated, by SIC code, the percentage of waste reported in the volatile categories in relation to the total waste volume re-SAI then compared these results with those of the State OAT study (Office of Appropriate Technology) 1981 - Alternative to the Land Disposal of Hazardous Wastes. Table 2-3 shows the results of the SAI analysis with the results of the OAT study. These results indicate that 36 percent of the waste in California consist of volatile materials other than water.

The volatility of a compound does not have a definition that can be used in air pollution studies. It is SAI's understanding that what is important in air pollution studies or regulations is the rate at which a pollutant evaporates into the air. The rate of evaporation that is considered important

or critical will depend on the volume of air "receiving" the pollutant. The rate of evaporation is classically calculated according to the physical chemistry of this phenomenon. The rate of evaporation is directly proportional to the partial pressure of the pollutant in solution (water in this study) and also directly proportional to the mass transfer coefficient. The product (multiplicative) of the partial pressure and the mass transfer coefficient yields the flux (not rate) of evaporation. By calculating the surface area of the solution exposed to the air, the rate of evaporation is obtained. Thus, four quantities are of importance in determining the rate of evaporation of a pollutant from water; these are

- (1) partial pressure (related to vapor pressure)
- (2) mass transfer coefficient (kinetics such as wind speed)
- (3) surface area of solution exposed to air
- (4) volume of air that will contain the pollutant.

By considering the above four quantities, a mass balance can be derived that predicts the mass of pollutant that will be in the air. Thus, volatility as it relates to partial pressure is only part of the prediction. and the partial pressure of a component in water is not a straight-forward prediction in itself.

The analysis of volatile components of the waste stream is limited by the gross assumptions that had to be made to perform this analysis. The assumptions included:

If a RCRA waste code indicated that a volatile material was present in the waste stream the entire waste stream was considered to be volatile.

- Although the relative volumes of waste by RCRA code are not totally reliable as was indicated in the earlier discussion of the Part A data base they were considered sufficiently reliable to permit this computation.
- The data on waste codes and volatility are sufficiently reliable to permit a judgment on the volatile nature of the waste stream.

The calculation that was used to obtain the relative volatility of waste streams was made by determining the sum of the volatile components over the total waste stream. An assumption of the composite waste stream was used to make this determination.

TABLE 2-3. WASTE STREAM VOLATILE COMPONENT BY INDUSTRIAL CATEGORY

SIC Code	!	Percent Volatil from Part A Data Base	OAT Estimates
07	Agricultural Services	1.3	5.5
13	Oil and Gas Extraction	2.5	1.8
20	Food and Kindred Products	0.6	0.4
24	Lumber and Wood Products	3.7	4.4
26	Paper and Allied Products	0.3	2.5
27	Printing and Publishing	1.6	0.5
28	Chemical and Allied Products	0.7	0.7
29	Petroleum and Coal Products	0.7	0.5
30	Rubber and Misc. Plastic Products	0.3	6.9
31	Leather Tanning and Finishing	1.0	0.4
32	Stone, Clay and Glass Products	1.1	5.1
33	Primary Metal Industries	2.6	0.4
34	Fabricated Metal Products	2.2	0.8
35	Machinery, Except Electrical	2.3	0.9
36	Electric and Electronic Equipment	0.2	1.8
37	Transportation Equipment	0.3	2.1
38	Instruments and Related Products	0.4	4.8
40	Railroad Transportation	0	1.4
42	Motor Freight Transportation	1.5	2.7
	and Warehouse or Trucking		
	Sanitary Service		
44	Water Transportation	1.9	0.2
45	Air Transportation	0.3	0.6
46	Pipelines except Natural Gas	3.7	0.3
49	Electric, Gas and Sanitary Service 2	.1 -	
51	Wholesale Trade Non-durable Items 3.	<b>-</b>	
73	Business Service	0.1	-
75	Auto Repair Service and Garage	3.4	-
96	Dept. of Food and Agriculture	0.2	-
99	Non-classifiable Establishments	1.4	
		36.7	44.2

### 2.4.3 <u>Volatile Inventory Summary</u>

SAI's assessment of the volatile component of the California hazardous waste inventory, indicates that 36 percent of the waste contains volatile compounds. This figure could overrepresent the volume of volatiles because the presence of one volatile compound in the waste stream results in the entire stream being considered volatile. The second part of this analysis was to evaluate the potential amount of volatile wastes currently disposed in California land fills. A comprehensive waste stream classification system was developed by the University of California, Davis (UCD) for use in their study of hazardous waste generation in California. The 94 categories comprising this system represent most of the waste streams generated in California.

Based on technical knowledge and experience concerning the waste streams listed (composition of the waste streams, volume of waste generated, disposal methods, and waste type, i.e., sludge, slurry, liquid, solid), 41 waste categories having the greatest potential for generating volatile organic air contaminants were selected (Table 2-4). Table 2-4 also provides UCD's original estimate of the quantity of waste generated and disposed of off-site statewide for each of these volatile organic material categories. waste generation estimates were based on two months (September, 1979 and May, 1980) of manifest data and the values in the table are projections made from these data. As can be seen from this table, the largest single waste stream is aqueous solutions with less than 10 percent organics (UCD #225), which accounts for 93,666 tons of material disposed annually. Oily wastes (UCD #281 to 289) comprises 28 percent of the total volatile waste disposed off-site. The source of these wastes streams is primarily the petroleum refining industry (SIC 29). While the total weight of the identified waste streams comprises almost 44 percent of the state's total offsite waste streams, it represents only a small fraction of the total waste amount generated and disposed of on-site (See Table 2-1).

TABLE 2-4. POTENTIAL VOLATILE WASTES DISPOSAL AT CLASS I

AND CLASS II-1 SITES IN CALIFORNIA.

		WASTE AMOUNTS		
UCD#	WASTE CATEGORY	TONS/YR	% OF STATE TOTAL	
165	Spent Catalysts	16,332	1.2	
211	Halogenated Solvents w/ Heavy Metals	450	0.03	
212	Halogenated Solvents w/ Other Metals	72	0.01	
213	Halogenated Solvents	6,924	0.51	
214	Non-Halogenated Solvents w/ Heavy Metals	1,524	0.11	
215	Non-Halogenated Solvents w/ Other Metals	1,236	0.09	
216	Non-Halogenated Solvents	9,558	0.70	
217	Unspecified Solvents	3,342	0.25	
221	Organic Liquid w/ Halogens & Metals (all kinds*)	2,598	0.19	
222	Organic Liquid w/ Halogens Only	2,658	0.20	
223	Organic Liquid w/ Heavy Metals Only	1,362	0.10	
224	Other Organic Liquids	3,480	0.26	
225	Aqueous Solution w/ Organic Residues, <10%	93,666	6.88	
227	Aqueous Solution w/ Organic Residues, >10%	14,976	1.10	
231	Organic Solids w/ Halogens	120	0.01	
232	Organic Solids w/out Halogens	576	0.04	
241	Pesticides and Wastes	69 <b>,</b> 480	5.10	
242	PCB and Material Containing PCB	1,374	0.10	
243	Pharmaceuticals and Wastes	36	0.00	
245	Off-Specification or Aged Organics	78	0.01	
248	Non-Halogenated Still Bottoms	486	0.04	
254	Adhesives and Glue	5 94	0.04	
255	Other Unspecified Organic Wastes	180	0.01	
281	Waste Oil and Mixed Oil	7,602	0.56	

TABLE 2-4 (Continued)

		WAS	TE AMOUNTS
UCD#	WASTE CATEGORY	TONS/YR	% OF STATE TOTAL
282	Oily Tank Bottoms	3,984	0.29
283	Mixtures of Oil, Sediment, Water	47,487	3.48
284	Acidic Oily Sludge	3,240	0.24
285	Alkaline Oily Sludge	11,346	0.84
286	API Separator Sludge	11,526	0.85
287	Oily Sludge	24,300	1.79
288	Oily Sludge w/ Heavy Metals	4,770	0.35
289	Mixtures of Uil, Gas w/ Water	28, 902	2.12
446	Degreasing Sludge	132	0.01
447	Tetraethyl Lead Sludge	18,822	1.38
454	Paint Sludge	36,810	2.71
457	Sludges w/ Organic Residues	7,608	0.56
512	Spill Clean up	366	0.03
513	Laboratory Waste Chemicals	2,676	0.20
514	Contaminated Soil and Sand	21,594	1.62
523	Tank Bottom Sediments	54,690	4.01
531	Contaminated Rags, Pallets	1,266	0.09
	TOTAL	518,223	47.7

<sup>\*</sup> It is assumed that the "all kinds" of metals category does not include "heavy metals." (Otherwise there would be double counting.)

Source: Stoddard et al., 1981

While the total mass of waste disposed of on- and off-site are significantly different (1.35 million tons/year vs. 44.4 million tons/year), the waste stream compositions should be similar. This is because industries dispose of their waste in both types of sites. Thus, the types of volatile waste streams accepted for treatment/disposal should be similar between the two types of sites.

#### 2.5 WASTE CLASSIFICATION SYSTEM

Even though hazardous waste streams are typically complicated mixtures, different systems can be established for classifying wastes into categories. A large number of classification systems have been developed, each usually designed for a particular purpose. For example, a classification system which established groups on the basis of ease of incineration would classify organics separately from inorganics, non-halogenated organics from halogenated organics, and high BTU organics from low BTU organics.

Some classification systems are primarily descriptive and their main purpose is to provide a general picture of the waste stream. For example, California's DOHS manifest system lists 16 general waste categories, but a more detailed listing of waste categories was developed by the University of California at Davis (UCD). These 16 waste categories are:

- acid solution
- alkaline solution
- pesticides
- paint sludge
- solvent
- tetraethyl lead
- brine
- chemical toilet waste

- tank bottom sediment
- oil
- drilling muds
- contaminated soil and sand
- cannery wastes
- latex waste
- mud and water
- other

Recently the manifest was changed to include 75 waste categories.

The UCD system, patterned after an earlier New York State study, contains 109 waste categories. The UCD categories that apply to wastes generated in California and are disposed in off-site landfills (according to the UCD study) are listed in Table 2-5. Also presented in this table are the quantities of wastes disposed off-site in each waste category and the percentage of the State total.

The UCD classification system provides a significant amount of additional information beyond that provided by the State's 16-group system. It is important to note, however, that the UCD category assignments are best estimates that were based on professional judgement, using information provided on the California manifest forms (including the 16 categories), process information, and any additional industry specific information. Ideally, analytical composition data would be used for each waste stream in order to make an assignment, but this type of analytical data is usually not available. This is because most manufacturing facilities consider waste stream composition data as proprietary information and as such the reliability or accuracy of the data is not always known.

Based on our review of available information, the most serious difficulty in the categorization of wastes and the assessment of risk is the lack of comprehensive and reliable analytical waste stream data. If these data were available, one could group wastes more precisely according to the physical and chemical properties that control their tendency to become airborne. However, if analytical data were available, the grouping of waste streams according to physical and chemical properties would <u>not</u> be a trivial procedure, due to the complex composition of most waste streams.

As can be seen from Table 2-5, about 1.3 million tons of waste are sent to Class I and II-1 facilities in California each year. According to a recent study by the California Office of Appropriate Technology this off-site disposal tonnage represents about 30% of the total of 5 million tons of hazardous waste generated each year, thus, most of the waste, about 70%, is

TABLE 2-5. SUMMARY OF HAZARDOUS WASTE QUANTITIES DISPOSED OF IN CLASS I AND CLASS II-1 FACILITIES BY UCD\* WASTE CATEGORY.

		HAZARDOUS WAS	STE AMOUNTS
UCD #	WASTE CATEGORY	TONS/YEAR <sup>1</sup>	% STATE TOTAL
111	ACIDIC SOLUTION WITH HEAVY METALS	74,298	5.46
112		10,530	0.78
113		24,720	1.82
121		17,790	1.31
122			2.84
123 131		23,184 5,832	1.71 0.43
132		5,268	0.39
133		2,256	0.17
141		24,120	1.78
142	· · · · · · · · · · · · · · · · · · ·	22,116	1.63
143	AQUEOUS SOLUTION WITH REACTIVE ANIONS	59 <b>,</b> 790	4.39
	(includes cyanides - 17%, fluorides - 42%,		
	sulfides - 16%, bromates - 20%,		
144	hypochlorites - 5%) OTHER AQUEOUS SULUTIONS	4,596	0.34
144	BRINE	35,892	2.64
151	INURGANIC SOLIDS	1,512	0.11
153		540	0.04
161	ASBESTOS AND WASTES	33,576	2.46
162	ALUMINUM OR TIN DROSS	12	0.00
165	SPENT CATALYSTS	16,332	1.20
167	OTHER UNIDENTIFIED INORGANIC WASTES	1,542	0.11
211	HALOGENATED SOLVENT WITH HEAVY METALS	450	0.03
212 213	HALOGENATED SOLVENT WITH OTHER METALS HALOGENATED SOLVENTS	72 6,924	0.01 0.51
213	NON-HALOGENATED SOLVENTS NON-HALOGENATED SOLVENT WITH HEAVY METALS	1,524	0.11
215	NON-HALOGENATED SOLVENT WITH OTHER METALS	1,236	0.09
216	NON-HALOGENATED SOLVENTS	9,558	0.70
217	UNSPECIFIED SOLVENTS	3,342	0.25
		-	

 $<sup>^{1}\</sup>mbox{Estimated}$  by extrapolating UCD data for 2 months and adding estimates for Big Blue Hills.

Source: California Office of Appropriate Technology, 1981

<sup>\*</sup>UCD = the University California, Davis

TABLE 2-5. SUMMARY OF HAZARDOUS WASTE QUANTITIES DISPOSED OF IN CLASS I AND CLASS II-1 FACILITIES BY UCD WASTE CATEGORY. (Continued)

		HAZARDOUS W	MASTE AMOUNTS
UCD			% STATE
#	WASTE CATEGORY	TUNS/YEAR	TOTAL
	,		
-			<del></del>
221	ORGANIC LIQUID WITH HALOGENS & METALS (ALL KINDS	2 5 98	0.19
222		2,658	
223		1,362	
224	OTHER ORGANIC LIQUIDS	3,480	0.26
225		93,666	
	LESS THAN 10%		
227	AQUEOUS SOLUTION WITH ORGANIC RESIDUES,	14,976	1.10
	GREATER THAN 10%		
231		120	
232		576	
241		69,480	5.10
242		1,374	0.10
243			0.00
244			0.11
245		78	
248		486	
251		11,100	
253		2,130	0.16
255 255	ADHESIVES AND GLUE OTHER UNSPECIFIED ORGANIC WASTES	5 94	0.04
261		1 020	0.01 0.30
	LATEX & WASTES	1 038	0.01 0.30 0.14
263		9.618	0.71
271		984	0.07
272			0.11
281		7,602	0.56
282		3,984	0.56 0.29
	MIXTURES OF OIL, SEDIMENTS & WATER	47,487	3.48
284	ACIDIC OILY SLUDGE	3,240	
	ALKALINE OILY SLUDGE	11,346	0.84
286	API SEPARATOR SLUDGE	11,526	0.85
287	OILY SLUDGE	24,300	1.79
288	OILY SLUDGE WITH HEAVY METALS	4,770	0.35
28 9		28,902	2.12
412	FILTER PRESS CAKE/SLUDGE	864	0.06
413	SCRUBBER SLUDGE	780	0.06
416	INK SLUDGE	1,152	0.08
417	ALUM & GYPS UM SLUDGE	156	0.01
431	HEAVY-METAL SLUDGE	64,512	4.74

TABLE 2-5. SUMMARY OF HAZARDOUS WASTE QUANTITIES DISPOSED OF IN CLASS I AND CLASS II-1 FACILITIES BY UCD. WASTE CATEGORY. (Continued)

			HAZARDOUS WAS	STE AMOUNTS
UCD #	WASTE CATEGORY		TONS/YEAR	% STATE TUTAL
433			19,194	1.41
441			21,738	1.60
442	PHOSPHATE SLUDGE		114	0.01
443	SULPHUR SLUDGE		32,706	2.41
445	PLATING/METAL FINISHING SLUDGE		6,276	0.46
446	DECREASING SLUDGE		132	0.01
447	TETRAETHYL LEAD SLUDGE		18,822	1.38
453	•		4,020	0.30
454			36,810	2.71
455	DYE SLUDGE		54	0.00
456			2,784	0.21
457			7,608	0.56
509			18	0.00
510			78,474	5.77
511			24,012	1.77
512			366 2. 676	0.03
	LABURATORY WASTE CHEMICALS		2,676	0.20 1.62
514 515			21,594	9.61
518	DRILLING MUD DUST COLLECTOR WASTE		130,782 174	9.61
519			2,634	0.19
521	SPENT CARTRIDGE FILTERS		2,034 60	0.00
	TANK BOTTOM SEDIMENTS		54 <b>,</b> 690	4.01
524			960	0.07
525	METAL DUST & MACHINING WASTE		936	0.07
526	CANNERY WASTE		732	0.05
527	MUD/SEDIMENT & WATER		19,890	1.46
531	CONTAMINATED RAGS, PALLETS		1,266	0.09
532			6,736	0.50
535	TOTALLY UNSPECIFIED WASTES		2,994	0.22
		TOTAL	1,359,883	100.00%

disposed of on-site. The UCD study conducted in 1981 on on-site/off-site disposal patterns developed another estimate of the extent of on-site disposal. This information is listed by SIC code in Table 2-6. The on-site data is for the industrial, business, and other generators of the State. The 1.3 million tons disposed off-site each year is also listed in Table 2-6 in SIC code. When compared in the same table it becomes obvious that the quantity of documented off-site disposal is only a fraction (3%) of the estimated quantity of on-site disposal. According to this study then, more than 45 million tons of hazardous waste are produced each year in California. With data for on-site disposal varying widely between different sources, the reader is cautioned in relying on the data except as a rough estimate.

The industries responsible for most of the off-site disposal are listed in Table 2-7, developed from data listed in Table 2-6\*. As can be seen from this table, the major contributors to off-site disposal in California are the petroleum industry (extraction and refining) and the chemical industry (including agricultural chemicals) which together make up two-thirds (65.9%) of the total, or about 857 thousand tons annually. Since most of the major contributors, (petroleum extraction and refining, and chemical production) are located in or near to major population centers such as Greater Los Angeles, Greater San Francisco, or Bakersfield, disposal from these industries is also near to the same centers of population. Table 2-8 lists the major population areas and their percentage of off-site disposal. Also, because these industries produce waste streams which are rich in organics and generally quite volatile, it can be assumed as a first estimate that their waste streams also represent the greatest contribution to air emissions and the greatest risk of adverse health effects to the surrounding population.

For example, from Table 2-8 it can be seen that East Bay, Los Angeles and Bakersfield represent most of the off-site disposal and that the San Francisco area as a whole is responsible for one-third of the State's off-site disposal.

<sup>\*</sup>This is based on OAT studies. Chapter 2 discusses the accuracy of OAT's estimated 40 million tons of hazardous waste generated annually.

TABLE 2-6. COMPARISON OF ON-SITE VS OFF-SITE DISPOSAL IN CALIFORNIA BY SIC GROUPS

		ON-SITE AMOUNTS		OFF-SITE AMOUNTS	
			#STATE		≴STATE
	SIC CLASSIFICATION	TONS/YEAR*	TOTAL	TONS/YEAR**	TOTAL
7	Agricultural Services	1.806	0.00	5,818	0.43
13	Oil & Gas Extraction	1,760	0.00	265,164	19.52
20	Food & Kindred Products	517	0.00	4,890	0.07
24	Lumber & Wood Products	16,251	0.04	990	0.07
26	Paper & Allied Products	48,837	0.11	10,242	0.75
27	Printing & Publishing	419	0.00	1,824	0.13
28	Chemicals & Allied Products	8,591,149	19.37	265,848	19.55
29	Petroleum & Coal Products	24,559,835	55.38	381,042	28.04
50	Rubber & Misc. Plastics Products	897	0.00	1,146	0.08
3 1	Leather Tanning & Finishing	51	0.00	11,694	0.86
2	Stone, Clay & glass Products	48,671	0.11	21.750	1:60
33	Primary Metal Industries	130,735	0.29	26,802	1.97
4	Fabricated Metal Products	143,174	0.32	64,266	4.73
5	Machinery, except Electrical	14,390	0.03	18,360	1.35
6	Electric & electronic Equipment	8,910,280	20.09	55,500	4.08
57	Tranportation Equipment	890,972	2.01	47,592	3.50
8	instruments & Related Products	374,660	0.84	7,740	0.57
10	Railroad Transportation	0	0.00	3,468	0.26
12	Trucking & Samitary Services	243,983	0.55	12,294	0.90
4	Water Transportation	1,380	0.00	1,578	0.12
5	Air Transportation	189	0.00	3,732	0.27
16	Pipelines, except Natural Gas	1,551	0.00	3,750	0.28
19	Electric, Gas & Samitary Services	118,271	0.27	69,270	5.10
51	Wholesale Trade-Nondurable Goods	4,868	0.01	2,172	0.16
73	Business Services	201,069	0.45	4,956	0.36
75	Auto Repair, Services & Garages	0	0.00	1,842	0.14
96	Dept. of Food & Agriculture	76	0.00	11,962	0.14
	Other Minor 0100-199 SIC Groups	3,691	0.01	1,200	0.09
	Other Minor 2000-3999 SIC Groups	872	0.00	894	0.07
	Other Minor 4000–9700 SIC Groups	39,987	0.09	5,680	0.42
	Generators with Unidentifiable SIC	0	0.00	29.796	2.19
00	Generators with UCD Augmented Codes	0	0.00	29,310	2.15
тот	'AI	44,350,341	100%	1,358,562	100%

<sup>\*</sup>Secause of the paucity of information available for on-site disposal this data should be used only as rough estimate.

<sup>\*\*</sup>Source: U.C.D. Study of hazardous waste generation and offsite and onsite disposal patterns in California, 1981.

TABLE 2-7. INDUSTRIES RESPONSIBLE FOR THE MOST OFF-SITE WASTE DISPOSAL IN CALIFORNIA.

INDUSTRY	% OFF-SITE DISPOSAL IN CALIFORNIA
Petroleum Refining	27.5
Oil and Gas Extractions	19.5
Chemical and Allied Products	18.9
Electric, Gas and Sanitary Services	5.0
Fabricated Metal Products	4.7
Electric and Electronics Equipment	4.1
Transportation Equipment	3.5
All other industries combined	16.8
TOTAL	100%

Source: OAT 1981

TABLE 2-8. CALIFORNIA POPULATION CENTERS CONTAINING MOST OF THE OFF-SITE DISPOSAL OF HAZARDOUS WASTE.

	WASTE AMOUNTS		
AREA	TONS/YEAR	%STATE TOTAL	
ast San Francisco Bay	287,270	21.1%	
os Angeles	268,230	19.7%	
akersfield	150,170	11.0%	
Sonoma	76,690	5.6%	
Fresno	72,800	5.3%	
Totals	855,160	62.7%	
an Francisco Bay area s a whole	455,160	33.3%	
(includes the East Bay,			
Sonoma, Peninsula, and			
South Bay areas)			

Source: OAT 1981

The University of California at Davis (UCD) identified 94 categories of wastes currently being disposed in off-site facilities. Data from this study allow the breakdown of off-site waste disposal by major industries and category of wastes which is listed in Table 2-9. It also allows for the identification of the counties receiving most of the state's hazardous waste. Four counties, Los Angeles, Contra Costa, Alameda, and Solano are responsible for 53 percent of the hazardous off-site waste disposal off-site in California.

#### 2.6 SUMMARY AND CONCLUSIONS

Currently, little accurate data exist to reliably assess the quantities, types and sources of hazardous wastes generated in California. In the last six years, government and industry studies and surveys have been conducted in an effort to characterize the State's hazardous waste management situation. Unfortunately, the reported data have not considered all aspects of the problem being reviewed by the California Air Resources Board, such as accurate volatile estimates, precise waste stream data and specific disposal techniques.

Cognizant of the inherent problems associated with the task, SAI attempted to utilize, to the extent possible, the existing data bases and sources of information relative to the State's hazardous waste management program. Information was extracted from the sources to determine the quantities of hazardous waste generated, and the percentage and types of volatile constituents in the statewide waste stream.

The initial efforts of this task required identification of all potential data sources. From these sources, the quantities of hazardous wastes generated in the State were estimated. The derived estimates were compared to previously generated data from the University of California - Davis (UC) study. Finally, estimations of the volatile emissions portion of the total waste stream were deduced.

TABLE 2-9. MAJOR INDUSTRIES, CATEGORIES AND COUNTIES WITH RESPECT TO OFF-SITE WASTE DISPOSAL IN CALIFORNIA.

	WASTE	AMOUNTS
	TONS/YEAR	%STATE TOTAL
jor Industries		
Petroleum and Coal Products	381	29.3
Oil and Gas Extraction	265	20.4
Chemicals and Allied Products	266	20.5
egories of Waste		
Drilling muds	131	10.1
Aqueous solutions of organics	109	8.4
Refinery flue-gas scrubber liquids	78	6.0
Acidic Solutions of heavy metals	74	5.6
Pesticide Wastes	69	5.3
or Counties	689	53.0
(Los Angeles, Alameda,		
Contra Costa and Solano)		

Source: University of California at Davis (UCD) 1982

The results of the investigation indicated that approximately 41,694,000 metric tons of hazardous wastes are generated annually in California. The finding was based primarily on the EPA Region IX Part A Permit Application data base and the State Board of Equalization records. This estimation of waste was comparable to the 44,500,000 tons estimated in the UCD study. Of the State's total annual waste stream, an estimated 36 percent contained volatile constituents. Similarly, this estimate approximated the results of the 1981 study conducted by California's Office of Appropriate Technology.

Although these estimations had several limitations due to the data sources, the values derived are considered reasonable. The data is also thought to be useful in making other determinations of hazardous waste management practices in the State. An inventory of toxic and hazardous waste is the first step in being able to regulate waste management practices. Once an inventory has been made, methods of regulating must then be considered. One method of regulating waste is to develop a categorical ranking system whereby under specific conditions specific management practices must be followed. One such ranking system is that tied to an assessment of risk to health of surrounding populations.

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# 2.8 APPENDIX

Conversion of RCRA Waste Codes to UCD Waste Codes

EPA CODE	UCD CODE	MATERIAL
U141		Isosafrole
U142	241	Kepone
U143	•	Lasiocarpine
U144	777/241	Lead acetate
U145	431	Lead phosphate
U146	111	Lead subacetate
U147	232	Maleic anhydride
U148		Maleic hydrazide
U149		Malononitrile
U150		Melphalan
U151	153	Mercury
U152	224	Methacrylonitrile
U153	224	Methanethiol
U154	216	Methanol
U155	224	Methapyrilene
U156	222	Methyl chlorocarbonate
U157	231	3-Methylcholanthrene
U158	241	4,4'-Methylene-bis-(2-chloroaniline)
U159	216	Methyl ethyl ketone (MEK) (1,T)
U160	216	Methyl ethyl ketone peroxide (R)
U161	216	Methyl isobutyl ketore
U162	224 *	Methyl methacrylate (R,T) N Methyl-N'-nitro-N-nitrosoguanidine
U163 U164	•	Methylthiouracil
U165	224	Naphthalene
U166	232	L,4-Naphthoquinone
U167	224	1-Naphthylamine
U168	*	2-Naphthylamine
<b>U</b> 169	224	Nitrobenzene (1,T)
U170	224	4-Nitrophenol
U171	224	2-Nitropropane (1)
U172	224	N-Nitrosodi-n-butylamine
U173	224	N-Nitrosodiethanolamine
U174	224	N-Nitrosodiethylamine
U175	224	N-Nitrosodi-n-propylamine
U176	Z24	N-Nitroso-n-ethylurea
U177	224 224	N-Nitroso-n-methylurea N-Nitroso-n-methylurethane
U178 U179	224	N-Nitrosopiperidine
U180	224	N-Nitrosopyrrolidine
U181	*	5-Nitro-o-toluidine
U132	*	Paraldehyde
U183	232	Pentachlorobenzene
U184	222	Pentachloroethane
U185	222	Pentachloronitrobenzene
U186	224	1,3-Pentadiene (1)
U187	*	Phenacetin
U188	224	Phenol
U189	153	Phosphorous sulfide (R)
<b>U</b> 190	232	Phthalic anhydride
	224	2-Picoline
U192	*	Pronamide 2-65

```
U193
                1,3-Propane sulfone
U194
                n-Propylamine (1)
U196 not present Pyridine
         224
U197
                Quinones
U200
                Reserpine .
         224
U201
                Resorcinol
U202
         700
                Saccharin
U203
                Safrole
         111
U204
                Selenious acid
U205
         537
                Selenium sulfide (R,T)
U206
                Streptozotocin
U207
         222
                1,2,4,5-Tetrachlorobenzene
         2225
U208
               -1,1,1,2-Tetrachloroethane
         222
U209
                1,1,2,2,-Tetrachloroethane
U210
         213
                Tetrachloroèthene
         213
U211
                Tetrachloromethane
U212
         222
                2,3,4,6 Tetrachlorophenol
U213
         224
                Tetrahydrofuran (1)
U214
         111
                Thallium (1) acetate
U215
         111
                Thallium (1) carbonate
U216
         111
                Thallium (1) chloride
U217
         111
                Thallium (1) nitrate
U218
        153
                Thioacetamide
U219
         153
                Thiourea
U220
         216
                Toluene
U221
         224
                Toluenediamine
U222
                o-Toluidine hydrochloride
U223
         224
                Toluene diisocyanate
                Toxaphene 2,4,5
U224
         241
U225
         222
                Tribromomethane
U226
         213
                1,1,1-Trichloroethane
U227
         213
                1,1,2-Trichloroethane
U228
         213
                Trichloroethene
U229
        213
                Trichlorofluoromethane
U230
         241
                2,4,5-Trichlorophenol
U231
        241
                2,4,6-Trichlorophenol
U232
         241
                2,4,5-Trichlorophenoxyacetic acid
U233
         241
                2,4,5-Trichlorophenoxypropionic acid
                alpha, alpha, alpha- Trichlorotuluene
U234
        224
                Trinitrobenzene (R,T)
U235
         241
                Tris(2,3-dibromopropyl) phosphate
U236
                Trypan blue
U237
                Uracil mustard
U238
        261
                Urethane
U239
        216
                Xylene
```

D000		
D001		•
D002 D003		
D003	111	Arsenic
D005	112	Barium
D006	111	Cadmium
D007	111	Chromium
D008	111	Lead
D009	111	Mercury - Selenium
D010 D011	111 111	Silver
D012	241	Endrin (1,2,3,4,10,10-hexachloro-1,7-epoxy-1,4,42,
244-		5,6,7,8,8a-octahydro-1,4-endo,endo-5,8-dimethano
		naphthalens.
D013	241	Lindane (1,2,3,4,5,6-hexachlorocyclohexane,
T) () T 4	247	gamma isomer. Methoxychlor (1,1,1-Trichloro-2,2-bis (p-metho-
D014	241	xyphenyl)ethane).
D015	241	Toxaphene (C <sub>10</sub> H <sub>10</sub> Cl <sub>8</sub> , Technical chlorinated
~~~		
D016	241	camphene, 67-69% chlorine). 2,4-D,(2,4-Dichlorophenoxyacetic acid)
D010 D017	241	2,4,5-TP Silvex (2,4,5-Trichlorophenoxypropionic
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		acid).
	•	
FOOL	215	The spent halogenated solvents used in degreasing,
FUUL	213	tetrachloroethylene, trichloroethylene, methylene
		chloride, 1,1,1-trichloroethane, carbon tetrachlo-
		ride, and the chlorinated fluorocarbons, and
		sludges from the recovery of these solvents in
F007	213	degreasing operations. The spent halogenated solvents, tetrachloroethylene.
F002	213	trichloroethylene, methylene chloride, trichloro-
		fluoromethane and the still bottoms from the recover
		of these solvents.
F003	216	The spent non-halgenated solvents, kylene, acetone,
		ethyl acetate, ethyl benzene, ethyl ether, n-butyl alcohol, cyclohexanone, and the still bottoms from
		the recovery of these solvents.
F004	216	The spent non-halogenated solvents, cresols and
¥ 0 0 4		cresylic acid, nitrobenzene, and the still bottoms
•		from the recovery of these solvents.
F005	215	The spent non-halogenated solvents, methanol,
		toluene, methyl ethyl ketone, methyl isobutyl ketone, carbon disulfide, isobutanol, pyridine
		and the still bottoms from the recovery of these
		solvents.
F006	431	Wastewater treatment sludges from electroplating
		operations

F007	132	Spent plating bath solutions from electroplating
F008	431,	operations Plating bath sludges from the bottom of plating
F009	111	baths from electroplating operations  Spent stripping and cleaning bath solutions from
F010	287	electroplating oe-rations Quenching bath sludge from oil baths from metal
F011	112	heat treating operations  Spent solutions from salt bath pot cleaning from
F012	433.	metal heat treating operations - Quenching wastewater treatment sludges from metal
F013	143	heat treating operations  Flotation tailings from selective flotation from mineral metals recovery operations
F014	143	Cyanidation wastewater treatment tailing pond sediment from mineral metals recovery operations
F015.	143	Spent cyanide bath solutions from mineral metals recovery operations
F016	143	Dewatered air pollution control scrubber sludges from coke ovens and blast furnaces
F017 F018	454 454	Paint residues generated from industrial painting Wastewater treatment sludges from industrial painting painting.

# Wood Preservation:

K001	4.57	Bottom sediment sludge from the treatment from
Inorgan	ic	wood preserving processes that use creosote and/or
pigment	s:	pentachlorophenol.
KOÖ2	431	Wastewater treatment sludge from the production
		of chrome yellow and orange pigments.
K003	431	Wastewater treatment sludge from the production
11000	. • -	of molybdate orange pigments.
K004	431	Wastewater treatment sludge from the production
X004	421	
	,	zinc yellow pigments.
X005	431	Wastewater treatment sludge from the production
		of chrome green pigments.
K006	431	Wastewater treatment sludge from the production
		of chrome oxide green pigments (anhydrous and
•		hydrated)
X007	431	Wastewater treatment sludge from the production
1007	,	of iron blue pigments.
X008	431	Oven residue from the production of chrome oxide
8008	4 J T	
		green pigments

Organic C	hemical	ls:
		Distillation bottoms from the production of
		acetaldehyde from ethylene.
K010 2	22· I	Distillation side cuts from the production of
	a	acetaldehyde from ethylene.
K011 2	25 1	Bottom stream from the wastewater stripper in
	1	the production of acrylonitrile.
K012 2		Still bottoms from the final purification of
		acrylonitrile.
K013 2		Bottom stream from the acetonitrile column in
		the production of acrylonitrile.
K014 2		Bottoms from the acetronitrile purification
	(	column in the production of acrylonitrile
K015 2		Still bottoms from the distillation of benzyl
	(	chloride.
K016 2	222 F	Heavy ends or distillation residues from the
	3	production of carbon tetrachloride.
K017 2		Heavy ends (still bottoms) from the purification
	(	column in the production of epichlorohydrin.
K018 2	222 g	Heavy ends from fractionation in ethyl chloride
	1	production.
K019 2	222	Heavy ends from the distillation of ethylene
	(	dichloride production.
K020 2	222	Heavy ends from the distillation of vinyl
		chloride in vinyl chloride monomer production.
K021 2	221 ,	Aqueous spent antimony catalyst waste from
-		fluoromethanes production.
K022 2	224 ]	Distillation bottom tars from the production
	•	of phenol/acetone from cumene.
K023 2	224 ]	Distillation light ends from the production of
	1	phthalic anhydride from naphthalene.
X024 2	248	Distillation bottoms from the production of
	]	prinatic annydrice from naprinatene.
K025 248,		Distillation bottoms from the production of
_	1	nitrobenzene by the nitration of benzene.
K026 2	224	Stripping still tails from the production of
	;	methyl ethyl pyridines.
X027 2	224	Centrifuge residue from toluene diisocyanate
_		production.
K028	222	Spent catalyst from the hydrochlorinator reactor
		in the production of 1,1,1-trichloroethane.
K029	222	Waste from the product stream stripper in the
	~ ~ ~	production of 1,1,1-trichloroethane.
X030	222	Column bottoms or heavy ends from the combined
		production of trichloroethylene and perchloro-
		ethylene.
Pesticide		n
K031 223		By-products salts generated in the production
K032 222	241	of MSMA and cacodylic acid.
XU32 222		Wastewater treatment sludge from the production of chlordane.
		2_60 `
		/=D4

**-**69

X033	222,241	Wastewater and scrib water from the chlorination
X034	222,241	of cyclopentadiene in the production of chlordane Filter solids from the filtration of hexachloro-
XU3+	·	cyclopentadiene in the production of chlordane.
K035	457,241	Wastewater treatment sludges generated in the
K036	241	production of creosote. Still bottoms from toluene reclamation distil-
		lation in the production of disulfcton.
X037	241	Wastewater treatment sludges from the production of disulfoton.
X038	241.	Wastewater from the washing and stripping of
٠.		phorate production.
X039	241	Filter cake from the filtration of diethylphosa
K040	241	phorodithoric acid in the production of phorate. Wastewater treatment sludge from the production
7040		of phorate.
K041	241	Wastewater treatment sludge from the production
K042	222,241	of toxaphene. Heavy ends or distillation residues from the
X-04-2	220,242	distillation of tetrachlorobenzene in the
		production of 2,4,5 T.
K043	222,241	2.6 Dichlorophenol waste from the production
		of 2,4-D.
	sives:	
K044	456	Wastewater treatment sludges from the manufacturing
X045	255	and processing of explosives.  Spent carbon from the treatment of wastewater
X043		containing explosives.
K046	457	Wastewater treatment sludges from the manufacturing
		formulation and loading of lead-based initiating compounds.
K047	225	Pink/red water from TNT operations.
	oleum Refi	
X048		Dissolved air flotation (DAF) flat from the
		petroleum refining industry.
K049	287	Slop oil emulsion solids from the petroleum refining industry.
K050	457	Heat exchanger bundle cleaning sludge from the
		petroleum refining industry.
K051	286	API separator sludge from the petroleum refining industry.
K052	447	Tank bottoms (leaded) from the petroleum refining
•		industry.
	her Tannir 251	ng Finishing: Chrome (blue) trimmings generated by the following
K053	201	subcategories of the leather tanning and finishing
		industry hair pulp/chrome tan/retan/wet finish,
		hair save/chrome tan/retan/wet finish, retan/
		wet finish no beamhouse, through the blue and shearing
		2-70

Seconda K069	ary Lead 431	l: Emission control dust/sludge from secondary lead smelting
Hazardo K070	ous Wast *	es From Specific Sources:  Woven fabric dying and finishing wastewater  treatment sludges.
K071	*	Mercury bearing sludges from brine treatment and mercury bearing brine purification muds from the mercury cell process in chlorine production.
K072	*	Wastewater treatment sludge from the diaphragm cell process using graphite anodes in the
K073	225	production of chlorine. Chlorinated hydrocarbon bearing wastes from the diaphragm cell process using graphite anodes in chlorine production.
K074	*	Wastewater treatment sludges from the production of TiO, pigment using chromium bearing ores by the chloride process.
K075	*	Wastewater treatment sludges from the production of TiO, pigment using chromium bearing ores by the sulfate process.
K076	*	Arsenic bearing sludges from the purification process in the production of antimony oxide.
K077	*	Antimony bearing wastewater treatment sludge from the production of antimony oxide.
K078	454	Solvent cleaning wastes from paint manufacturing.
K079	454	Water cleaning wastes from paint manufacturing.
K080	454	Caustic cleaning wastes from paint manufacturing.
K081	454	Wastewater treatment sludges from paint manufac-
XOO1		turing.
K082	454	Air pollution control sludges from paint
1002		manufacturing.
K083	*	Still bottoms from aniline production.
K084	*	Arsenic or organo-arsenic containing wastewater
2004		treatment sludges from the production of veterinary pharmaceuticals.
K085	*	Distillation residue from the separation or chlorobenzenes in the production of chlorobenzenes.
X086	416	Sludges, wastes from tub washers (ink formulation).
X087	*	Coking: Decanter tank tar/pitch/sludge.
K088	*	Spent potliners (cathodes) from primary aluminum production.
K089	*	Lead bearing wastewater treatment sludges from gray iron foundries.
K090	*	Emission control dust/sludge from ferro-chromium- silicon production.
K091	*	Emission control dust/sludge from ferro-chrome production.

K054	251	Chrome (blue) shavings generated by the
		following subcategories of the leather tanning
		and finishing industry: hair pulp/chrome tan/
		mater / wat finish bein some /chrome tan/
	•	retan/ wet finish; hair save/chrome tan/retan/
		wet finish, retan/wet finish, no beamhouse;
		through the blue; and shearing.
K055	251	Buffing dust generated by the following sub-
		categories of the leather tanning and finishing
		industry; hair pulp/chrome tan/retan/wet finish;
		hair save/chrome tan/retan/wet finish; retan/
		wet finish; retan/wet finish, no beamhouse,
	•	
-		and through the blue.
K056	251	Sewer screenings generated by the following
		subcategories of the leather tanning and
		finishing industry hair pulp/chrome tan/retan/
		wet finish; hair save/chrome tam/retam/wet
		finish; retan/wet finish, no beamhouse, through
70057	257	the blue; and shearing.
X057	251	Wastewater treatment sludges generated by the
		following subcategories of the leather tanning
K058	251.	Wastewater treatment sludges generated by the
		following subcategories of the leather tanning.
		and finishing industry; hair pulp/chrome tan/
		retan/wet finish; hair save/chrome tan/retan/
*** 0 = 0	252	wet finish; and through the blue.
K059	251	Wastewater treatment sludges generated by the
	-	following subcategory of the leather tanning
		and finishing industry, hair save/non-chrome
		tan/retan/wet finish.
		•
Iron and	d Steel	
X060	143	Ammonia still lime sludge from coking operations.
K061	431	Emission control dust/sludge from the electric 7
XOOT	754	furnace production of steel.
2000		
K062	111	Spent pickle liguor from steel finishing
		operations.
K063	431	Sludge from lime treatment of spent pickle
		liquor from steel finishing operations.
Primary	Cooper	
	431	Acid plant blowdown slurry/sludge resulting from
X004	*****	the thickening of blowdown slurry from primary
_	_	copper production.
Primary	Lead,	
K065	431	Surface impoundment solids contained in and dredged
		from surface impoundments at primary lead
		smelting facilities.
D-i		SWOTPTIE TROUTEDANS
Primary		*
K066	431	Ammonia still lime sludge from coking operations.
K067	431	Electrolytic anode slimes/sludges from primary
	•	zine production
K068	431	Cadmium plant leach residue (iron oxide) from
		primary zinc production.
		France, branches,

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Emission control dust/sludge. from ferro-manganese
K092
                production.
K093
K094
               -3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin
P001
                and salts.
      224.225
                1-Acetyl-2-thiourea
P002
        224
                Acrolein
\Sigma nn\sigma
        241
                Aldrin
P004
        224
                Allyl alcohol
P005
                Aluminum phosphide (R)
        153
P006
                5-(Aminomethyl)-3-isoxazolol
        241
P007
        241
                4 Aminopyridine
P008
      225,227
                Ammonium picrate (R)
P009
        131
                Arsenic acid
P010
         111
                Arsenic pentoxide
P011
         111
                Arsenic trioxide
P012
                Barium cyanide
        143
P013
                Benzenethiol
P014
         525
                Berylium dust
P015
                Bis(chloromethyl) ether
P016
                Bromoacetone
P017
       *alkaloidBrucine
P018
                2-Butanone peroxide
         224
P019
                2 see Butyl 4.6 dinitrophenol
         241
P020
         241
                Calcium cyanide
POZ1
         224
                Carbon disulfide
P022
                Chloroacetaldehyde
         222
P023
                 p Chloroaniline
         222
P024
                 1-(p Chlorobenzoyl) 5 methoxy-2-methylindole
 P0.25
                 3-acetic acid-
                 1 (o-Chlorophenyl)thiourea
         222
 P026
                 3-Chloropropionitrile
         222
 P027
                 alpha-Chlorotoluene
         222
 P028
                 Copper cyanide
         143
 P029
 P030
         143
                 Cyanides
         ÷
                 Cyanogen
 P031
                 Cyanogen bromide
         153
 P032
                 Cyanogen chloride
 P033
                 2-Cyclohexyl-4,6-dinitrophenol
         241
 P034
                 2,4-Dichlorophenoxyacetic acid (2,4-D)
         241
 P035
 P036
                 Dichlorophenylarsine
```

Dieldrin

Diethylarsine

P037

P038

241

241

```
P039
        241
                0,0-Diethyl-S-(2-(ethylthio)ethyl)ester of.
                phosphorothicic acid.
        241
P040
                0,0-Diethyl-0-(2-pyrazinyl)phosphorothioate
        241-
P041
                0,0-Diethyl phosphoric acid, 0-p-nitrophenyl
P042
                3,4-Dihydroxy-alpha-(methylamino)-methyl benzyl
                alcohol.
P043
                Di-isopropylfluorophosphate
        241
P044
        241
                Dimethoate
P045
                3,3-Dimethyl-1-(methyltio)-2-butanone-0-[(methyl-
                amino) carbonyl] oxime
P046
                alpha, alpha-Dimethylphenethylamine
        241
P047
                4,6-Dimitro-o-cresol and salts
P048
         241
                2,4-Dinitrophenol
P049
        241
                2.4-Dithiobiuret
        241
P050
                Endosulfan
        241
P051
                Endrin
P052
                Ethylcyanie
P053
         224
                Ethylenediamine
P054
         224
                Ethyleneimine
P055
         143
                Ferric cyanide
P056
                Fluorine
P057
         241
                2-Fluoroacetamide
P058
         241
                Fluoroacetic acid, sodium salt
P059
         241
                Heptachlor
                1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-
P060
                1,4:5,8-endo, endo-dimethanonaphthalene.
         222
P061
                Hexachloropropens
P062
                Hexaethyl tetraphosphate
P063
         143
                Hydrocyanic acid
                Isocyanic acid, methyl ester
P064
         153
                Mercury fulminate
P065
         241
P066
                Methomyl
P067
                2-Methylaziridine
         232
P058
                Methyl hydrazine
         224
P069
                2-Methyllactonitrile
                2-Methyl-2 (methylthio) propional dehyde-o-
P070
                (methylcarbonyl) oxime.
         241
                Methyl parathion
P071
                1-Naphthy1-2-thiourea
P072
P073
                Nickel carbonyl
                Nickel cyanide
P074
         143
P075
         241
                Nicotine and salts
                Nitric oxide
P076
         224
P077
                p-Nitroaniline
P078
         532
                Nitrogen dioxide
P079
                Nitrogen peroxide
         153
P089
                Nitrogen tetroxide
                Nitroglycerine (R)
P081
         224
                N-Nitrosodimethylamine
P082
                N-Nitrosodiphenylamine
P083
```

```
N-Nitrosomethylvinylamine
P084
               Octamethylpyrophosphoramide
P085
        241
               Oleyl alcohol condensed with 2 moles ethylene
P086
        224
               oxide.
P037
        111
               Osmium tetroxide
                7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic
POS8
               acid
               Parathion
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## CHAPTER 3

PETROLEUM INDUSTRY LANDFARM WASTE CHARACTERIZATION

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# CHAPTER 3 PETROLEUM INDUSTRY LANDFARM WASTE CHARACTERIZATION

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#### CHAPTER 3

#### PETROLEUM INDUSTRY LANDFARM WASTE CHARACTERIZATION

The Resource Conservation and Recovery Act (RCRA) passed in 1976 limits industries' alternatives for disposal of hazardous waste materials. Because of these limitations, industry is seeking alternative approaches to handle waste disposal economically. Twenty-one such facilities in California have recorded interest in one such alternative, landfarming, by notifying the U.S. EPA of either current activity or plans of future activity using this disposal technology. Of these 21 facilities only three are currently using landfarming as a disposal practice. Two of these facilities are operated by Chevron Oil; one is located in El Segundo, CA, the other in the San Francisco Bay Area (Richmond, CA). The third facility, Union Oil Company of California, is also located in the San Francisco Bay Area (Rodeo, CA). These three facilities were sampled for different waste types which the refineries currently dispose of through the practice of landfarming. This study was designed to characterize the waste constituents, both organic and inorganic, in material that is being landfarmed.

Landfarming, a technique also known as landspreading, sludge farming and solid incorporation, has been practiced by petroleum refineries since the mid 1950's. This waste treatment technique relies upon the action of microorganisms that are naturally occurring in the soil to biodegrade organic wastes. Landspreading is suitable for limited applications and has traditionally included separator sludge, emulsion solids, cooling water sludges and tank bottoms. In California, landspreading is most often used for disposal of the oily wastes from petroleum refineries. The biological degradation of organics in the land produces carbon dioxide, water and ash which are not considered pollutants. Advantages claimed by proponents of landfarming include minimum energy required to dispose of the waste, the process is relatively odorless and the procedure can be repeated safely at frequent intervals.

Landspreading is recognized as a potential source of air pollution as volatile products are produced by some oily-waste degradation. Also, increasing concentrations of trace metals have been reported in the top 12 inches of the soil in landspreading areas.

The objective of this study was to characterize as many of the individual waste types as were available from the three separate petroleum refineries that are actively using the landfarming treatment/disposal technique. The characterization included both organic and inorganic constituents with an effort being placed on estimating atmospheric emissions of volatile compounds from the landfarm.

#### 3.1 EXPERIMENTAL METHODS

#### 3.1.1 Field Sampling Activities

This section of the report describes SAI's field sampling activities which resulted in the acquisition of four petroleum refinery waste sample types. These sample types included oil contaminated soils, various types of refinery waste sludges (which includes biosludges, API separator sludge, and dissolved air flotation sludges), oil containing algae skimmings, and a tank bottom sample. Three California refineries were sampled including the Union Uil Refinery in Rodeo, Chevron Refinery in Richmond, and Chevron Refinery in El Segundo. Samples of biosludge (originated from activated sludge from refinery wastewater treatment), API separator sludge (produced in the initial recovery of oily materials from liquids and wastewaters collected from various processes throughout the refinery), and Dissolved Air Flotation (DAF) sludge (originated from the recovery of oils from refinery waste treatment) were collected at the Union Oil Refinery on March 28, 1983. All samples were taken under supervision of refinery personnel. These samples are typical of samples taken routinely by refinery personnel.

Biosludge is transferred to ten holding areas where water is separated from the sludge by gravity filtration through sand. The sludge is

allowed to weather and then is applied to the landfarm. Samples of biosludge at various stages of weathering were composited from four of the holding areas. The compositing was performed using a hand shovel and a large stainless steel bucket. After sampling the four holding areas, the sludge was thoroughly mixed in the bucket and transferred to sample containers.

API separator sludge was also composited using a hand shovel and a stainless steel bucket. The sludge was scraped from metal blades in the separator device, and then mixed in the bucket before being transferred to sample containers.

DAF sludge was sampled using a 500 ml teflon jar attached to a long pole, which was dipped into the aqueous sludge. Compositing was completed in a stainless steel bucket where the DAF was mixed and then transferred to sample containers.

Samples of contaminated soils and algae skimmings were collected from the Chevron Refinery in Richmond on March 29, 1983. Two soil samples were collected; one from the Hazardous Waste Storage Area and the other from the San Pablo Tank Farm. Each of the soils was composited using the hand shovel for sampling and a stainless steel bucket for mixing. The samples were split into the appropriate containers for transport to the lab for analysis.

The oil contaminated algae skimmings were sampled from one of the "Baker Boxes" used as storage containers for the waste. The sample was obtained from a drain tube located at the bottom of the container. The sample was mixed in a stainless steel bucket and was then transferred to the appropriate containers.

A tank bottom sample was collected by Chevron-Richmond personnel and was sent to SAI in a metal can for analysis.

Samples of Induced Air Flotation (IAF) sludge and DAF sludge were collected at the Chevron Refinery in El Segundo on March 30, 1983. A vacuum

truck was used to remove the DAF from its storage tank. Following the removal of a partial truck load of waste from the tank, the DAF sludge was sampled from the drain line exiting the storage tank which had fed into the truck. This sample was mixed in a stainless steel bucket and was transferred to appropriate containers for transport to the lab. A COLIWASA (composite liquid waste sampler) was used to sample IAF sludge from its storage tank. The storage tank actually contained a mixture of IAF sludge, DAF sludge, and slop oil emulsions. The COLIWASA was lowered through the top of the storage tank to a depth of about 2 feet beneath the surface of the waste. The sample was mixed and transferred to appropriate containers.

The sample containers used were one liter amber glass jars for organics analyses and one liter teflon jars for metals analyses. Prior to use, the teflon jars were soap and water washed followed by acid cleaning using 3N  $\mathrm{HNO}_3$ , and the glass jars were soap and water washed followed by oven drying. After collection, samples were stored in an ice chest until returned to the lab where they were refrigerated (4 $^{0}\mathrm{C}$ ) until time of analysis.

#### 3.1.2 Sample Analyses

Samples of refinery waste were analyzed for the following parameters: oil and grease, total suspended solids and total dissolved solids, percent moisture, heat of combustion, the 13 EPA Priority Pollutant Trace Metals, EPA Priority Pollutant Volatile Organics, EPA Acid and Base/Neutral Priority Pollutant Organic Compounds, chlorinated hydrocarbons and pesticides, PCBs, and petroleum hydrocarbons. This section of the report describes the methods used in these analyses. An attempt was also made to analyze the samples for total cyanides and total phenols; however, both of these methods require an initial reflux-distillation step. In the method for total cyanides the distillation releases cyanide as hydrocyanic acid from cyanide complexes, and in the phenols method, the distillation removes interferring materials. During sample workup using both of the methods, samples boiled over rendering the

distillates useless. The methods were subsequently abandoned due to the instability of the analytes and the lack of preservatives in the samples.

Whole refinery waste samples were stored at  $4^{\circ}$ C after they were assigned unique in-house sample identification numbers. They remained refrigerated until time for further sample processing as required by the analytical protocols.

#### Oil and Grease

The method used is a modification of EPA method 413.1 (EPA, March 1979) for total recoverable oil and grease. This procedure measures the methylene chloride extractable matter (relatively non-volatile hydrocarbons) from each of the refinery wastes. The lighter more volatile hydrocarbons are not measured by this method as they are lost in the solvent removal operation. Also, materials which are not soluble in methylene chloride are not measured by the method.

Each sample was analyzed for oil and grease by acidifying one liter of sample (or an appropriate portion of sample diluted to one liter with deionized water) to a pH < 2 with 6N HCl. Following acidification the sample was transferred to a separatory funnel and extracted with 60 ml of methylene chloride. The solvent layer was removed, and the methylene chloride extraction was repeated two more times. The combined methylene chloride extracts were collected in a pre-weighed beaker. The methylene chloride was evaporated from the sample by gentle heating on a hot plate. The sample was cooled and the beaker was weighed.

#### Total Suspended Solids and Total Dissolved Solids

The method used for total suspended solids (TSS) was EPA method 160.2 (EPA, March 1979) for non-filterable residue. For total dissolved solids (TDS) EPA method 160.1 (EPA, March 1979) for filterable residue was used. The

two methods can be combined and run on the same sample aliquot. TSS and TDS were determined using 10~ml of each of the aqueous samples. The method was applied to solid samples and sludges by combining approximately 0.5~g of sample with 10~ml of deionized water. The resultant mixture was treated as an aqueous sample.

Each sample was mixed and an appropriate aliquot was removed and filtered through a pre-weighed glass fiber filter. TSS were determined by drying the residue retained on the filter to constant weight at  $100^{\circ}\text{C}$ . TDS were determined by evaporating and drying the filtrate from the TSS determination to a constant weight at  $180^{\circ}\text{C}$ .

#### Percent Moisture

Percent moisture was determined on the waste samples using two methods. The first method involved transferring approximately  $10~\rm g$  wet sample into a pre-weighed aluminum pan and then re-weighing the pan. The sample was dried in an oven at  $100-105^{\rm O}{\rm C}$  to a constant weight. The loss in sample weight represented the water content of the sample.

The second method involved transferring approximately 50 g of wet sample to a pre-weighed polypropylene jar and re-weighing to obtain the wet weight of the sample. The wet sample aliquots were taken to a constant dry weight by freeze drying. Again the loss in sample weight represented the water content of the sample.

#### Heat of Combustion

The heat of combustion was determined for each sample using ASTM method D-240. The method entails measuring the temperature increase of water surrounding the combustion vessel after combusting a known weight of the sample.

Approximately 1 g of sample was weighed into the combustion vessel or bomb. A fuse wire was placed into the bomb, 1 ml of water was added to the bottom of the bomb, and the bomb was closed. Next the bomb was charged with oxygen to 30 atmospheres. The bomb was then placed in 2 kilograms of water contained in a bucket which had a water jacket surrounding it. The temperature of the water in the bucket and the jacket were allowed to equilibrate. The bomb was fired off by applying an electrical charge to the fuse wire. As the temperature of the water in the bucket increased, hot water was added to the jacket to keep its temperature equal to that of the bucket water. The temperatures of the water in the bucket and the jacket were recorded each minute until three successive readings showed no further change  $(\underline{+}\ 0.002^{\circ}\mathrm{F})$ . Benzoic acid was used as the standard to calibrate the bomb.

## Priority Pollutant Trace Metals

The refinery waste samples were analyzed for the 13 EPA Priority Pollutant trace metals including Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, T1, and Zn. All labware used in the analyses was cleaned in 3N  $\mathrm{HNO}_3$  for a minimum of 48 hours followed by rinsing and soaking in deionized water. All of the initial sample handling was performed in a polyethylene hood to minimize the chance for atmospheric contamination. The analytical scheme is summarized in Figure 3-1 and explained in detail below. The initial sample preparation for analysis of all metals except Hg was as follows. Following the freeze drying process, the samples were ground to a homogenous powder using a mixer-mill. Approximately 0.5 grams of dry powdered sample was then weighed into quartz sample boats for low temperature ashing using a  ${\sf CF_4/0_2}$  plasma. The ashed samples were quantitatively transferred to tall form beakers, and  $10\,$ ml of double distilled  $\mathrm{HNO}_3$  were added. The samples were taken to dryness on a hot plate and were then charred. Next an additional 5 ml of  $\mathrm{HNO}_3$  were added to the samples followed by heating to dissolve the sample residue. The samples were cooled and 2 ml of 30%  $\rm H_2O_2$  (ULTREX) were added. The samples were again heated until the oxidative frothing of the peroxide ceased. Then the samples were cooled and diluted to 50 ml volume with deionized H $_2$ U. The

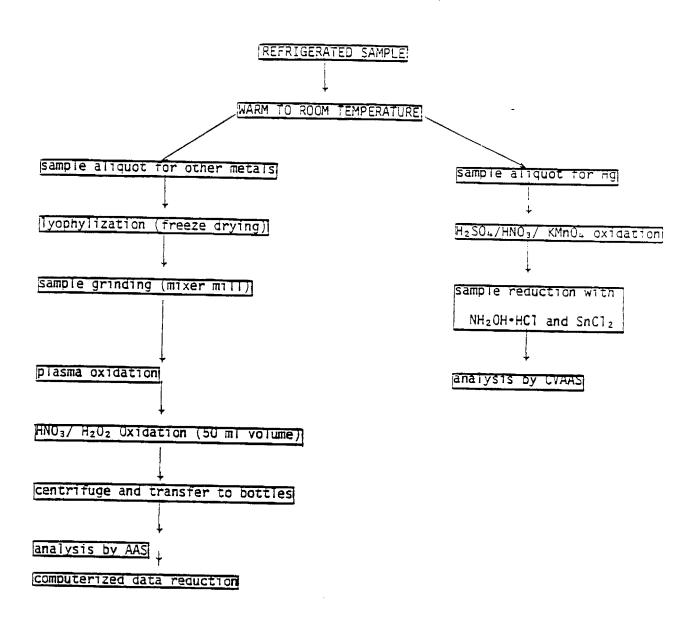


FIGURE 3-1. Analytical Scheme for Trace Metals in Refinery Waste Samples.

samples were centrifuged to remove any remaining solid material and the supernatants were analyzed by atomic absorption spectroscopy (AAS) using flame and graphite furnace techniques as described below.

The initial sample treatment for analysis of Hg was as follows. Approximately 2 g aliquots of each wet sample were transferred to a borosilicate bottle. Then 5 ml of double distilled  $\mathrm{HNO}_3$  and 5 ml of Hg free  $\mathrm{H_2SO}_4$  were added, and the samples were heated in a 95°C water bath for two hours. The samples were cooled and  $\mathrm{KMnO}_4$  was added until the purple color persisted. The samples were heated again for one hour, and were then cooled and refrigerated until analyzed as described below using cold vapor atomic absorption spectroscopy (CVAAS).

Samples treated for metals except Hg were analyzed using a Perkin-Elmer 603 Atomic Absorbtion Spectrometer equipped with air/C $_2$ H $_2$  and N $_2$ O/C $_2$ H $_2$  burner heads, an HGA-2200 graphite furnace, an AS-1 auto sampler, and a deuterium (D $_2$ ) background corrector. The D $_2$  background corrector was used on all analyses except for As and Se. The analytical wavelengths used for As and Se (194 and 196 nm respectively) are below the range of the D $_2$ . When performing graphite furnace analyses for As and Se, aliquots of the samples were mixed evenly with a 2000 ppm solution of Ni as Ni(NO $_3$ ) $_2$  to prevent pre-atomization of the samples. The instrument was routinely calibrated with a set of working standards which bracketed the metal concentrations in the samples. The working standards were prepared from commercially available 1000 ppm stock standards. In addition, the method of standard additions was performed routinely to compensate for the complex sample matrices. Instrument operating conditions are listed in Tables 3-1 and 3-2 for graphite furnace and flame analyses, respectively.

Samples treated for Hg were analyzed using a Laboratory Data Control 1234 Mercury Monitor. Prior to the analysis a 10 percent solution of NH $_2$ OH $_{\odot}$ HCl in 10 percent NaCl was added to each sample to reduce the excess KMnO $_4$ . Mercury in the sample solutions was reduced to the elemental state by

INSTRUMENT OPERATING CONDITIONS AND DETECTION LIMITS FOR METALS ANALYZED BY FLAMELESS (GRAPHITE FURNACE) ATOMIC ABSORPTION SPECTROPHOTOMETRY TABLE 3-1.

Additional Comments	$\mathbb{D}_2$ correction	Ni(NO3)2 matrix NoD2 correction	$ extsf{D}_2$ correction	O <sub>2</sub> correction	$\mathbf{0_2}$ correction	$0_2$ correction	$ extsf{D}_2$ correction
Instrument Detection Limit (ppb)	0.05	2	0.1	0.1	0.5	0.5	1.0
Furnace Conditions	Dry:110°c, 22 sec. Char: 400°c, 22 sec. Atomize: 2700°c,	Dry: 110°c, 30 sec. Char: 1200°c, 30 sec. Atomize: 2700°c,	Dry: 110°c, 22 sec. Char: 1200°c, 22 sec. Atomize: 2800°c,	Dry: 110°c, 22 sec. Char: 350°c, 22 sec. Atomize: 2100°c,	Dry: 110°c, 22 sec. Char: 1100°c, 22 sec. Atomize: 2700°c,	Dry: 110°c, 22 sec. Char; 900°c, 22 sec. Atomize: 2700°c,	Dry: 110°c, 30 sec. Char: 1100°c, 26 sec. Atomize: 2700°c, 8 sec.
Gas	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 30)	Ar (3 sec, normal flow, 40)	Ar (3 sec, normal flow, 65)
Injection Volume (με)	20	20	20	10	20	20	20
Slit Width (nm)	0.7	0.7	0.7	0.7	0.7	0.7	0.2
Lamp Currents (mA)	æ	18	14	4	∞	10	31
Wave Length (nm)	328.1	193.7	234.9	228.8	357.9	324.7	232
Element		As	B e	PS	5	ਤੋ	Ξ

INSTRUMENT OPERATING CONDITIONS AND DETECTION LIMITS FOR METALS ANALYZED BY FLAMELESS (GRAPHITE FURNACE) ATOMIC ABSORPTION SPECTROPHOTOMETRY(CONTINUED) TABLE 3-1.

Additional Comments	$\mathcal{L}_2$ correction	$ extsf{D}_2$ correction	Ni(NO <sub>2</sub> ) matrix No D <sub>2</sub> correction	D <sub>2</sub> correction	$egin{array}{l} B_2 & correction \\ Environmental \\ Contamination \end{array}$	Cold vapor analysis	
Instrument Detection Limit (ppb)	0.5	0.5	ø	0.5	 	0.5α	
Furnace Conditions	Dry: 110°c, 22 sec. Char: 750°c, 22 sec. Atomize: 2300°c,	Dry: 110°c, 30 sec. Char: 900°c, 26 sec. Atomize: 2700°c,	Dry: 110°c, 30 sec. Char: 1200°c, 26 sec. Atomize: 2700°c,	Dry: 110°c, 22 sec. Char: 400°c, 22 sec. Atomize: 2300°c,	Dry: 110°c, 22 sec. Char: 500°c, 22 sec. Atomize: 2500°c,	•	
Gas	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 20)	Ar (3 sec, normal flow, 20)	ı	
Injection Volume (με)	20	20	20	20	10	I	) g. nn tter).
Slit Width (nm)	0.7	0.2	0.7	0.7	0.7	1	e weight of 1.0 ed the detectionse bet
Lamp Currents (mA)	10	20	9	20		ţ	αDetection limit based on a sample weight of 1.0 g. If a greater sample weight is used the detection limit will correspondingly decrease (become better).
Wave Length (rm)	283.3	217.6	196	276.8	213.9	254	αDetection limi If a greater s limit will cor
Element	Pb	gs G	⊛ 3-11	E	Zn	Нĝ	

TABLE 3-2. INSTRUMENT OPERATING CONDITIONS AND DETECTION LIMITS FOR METALS ANALYZED BY FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

Element	Wave Length (nm)	Lamp Currents (mA)	Slit Width (nm)	Gas Oxidant/Fuel	Flame Type	Instrument Detection Limit (ppm)	Additional Commen <b>s</b>
Ag	328.1	æ	0.7	Air/C <sub>2</sub> H <sub>2</sub>	Oxidizing	0.01	D <sub>2</sub> correction
	193.7	18	0.7	Air/ C <sub>2</sub> H <sub>2</sub>	Reducing	0.5	Ni(NO <sub>3</sub> ) <sub>2</sub> matrix No D <sub>2</sub> correction
Ве	234.9	14	0.7	N <sub>2</sub> 0/C <sub>2</sub> H <sub>2</sub>	Reducing	0.005	$0_2$ correction
9 1 C	228.8	4	0.7	Air/C <sub>2</sub> H <sub>2</sub>	Oxidizing	0.01	$O_2$ correction
٠ ک	357.9	. 8	0.7	Air/C <sub>2</sub> H <sub>2</sub>	Reducing	0.03	$D_2$ correction
Cu	324.7	10	0.7	Air/C <sub>2</sub> H <sub>2</sub>	Oxidizing	0.04	$\mathtt{D}_2$ correction
Z	232	15	0.2	Air/C <sub>2</sub> H <sub>2</sub>	Oxidizing	0.1	$D_2$ correction
РЬ	283.3	10	0.7	Air/C <sub>2</sub> H <sub>2</sub>	Oxidizing	0.2	$D_2$ correction
Sp	217.6	20	0.2	Air/C <sub>2</sub> H <sub>2</sub>	Oxidizing	0.2	$D_2$ correction
Se	196	16	0.7	Air/C <sub>2</sub> H <sub>2</sub>	Oxidizing	0.3	Ni(NO <sub>3</sub> ) <sub>2</sub> matrix No D <sub>2</sub> correction
		_	-	_	•	_	

TABLE 3-2. INSTRUMENT OPERATING CONDITIONS AND DETECTION LIMITS FOR METALS ANALYZED BY FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY (CONTINUED)

Additional Comment	$0_2$ correction	D <sub>2</sub> correction Environmental Contamination		•		
Instrument Detection Limit (ppm)	0.2	0.015				
Flame Type	Oxidizing	0xidizing				
Gas Oxidant/Fuel	Air/C <sub>2</sub> H <sub>2</sub>	Air/C <sub>2</sub> H <sub>2</sub>				
Slit Width (nm)	0.7	0.7				
Lamp Currents (mA)	50		-			 
Wave Length (nm)	276.8	213.9				
Element	F	uz ,	2_12			

addition of a 20 percent solution of  ${\rm SnCl}_2$  in 3N HCl and then purged with nitrogen through the instrument described above. As with the other metals, working standards were prepared from a commercially available 1000 ppm Hg standard, and the instrument was calibrated with these standards. Standard additions were also performed on the samples.

#### EPA Priority Pollutant Volatile Organics

Aliquots of each of the refinery waste samples were transferred to 40 ml glass vials equipped with teflon lined septa immediately after arriving at the laboratory. These VOA vials were stored at  $4^{\circ}$ C until time of analysis. The samples filled the vials such that no air-space was present when capped. Purge and trap methodology was used to analyze each of the samples for volatile organic compounds.

The samples were prepared by tranferring a 10 gram aliquot to a modified purge chamber of a Tekmar LSC-2 Liquid Sample Concentrator. This was followed by the addition of 10 mls of organic-free water containing the appropriate internal standards and surrogate standards. The purge chamber was heated to  $55^{\circ}$ C, and the sample was then purged with inert gas. The volatile organics were transferred from the aqueous phase into the gaseous phase where they were passed through a sorbent bed (Tenax GC) designed to trap out the organic volatiles. After purging was completed, the Tenax trap was backflushed while being rapidly heated in order to thermally desorb the components into the inlet of a gas chromatograph. The components were separated via the gas chromatograph and detected using a mass spectrometer which was used to provide both qualitative and quantitative information.

Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, the purging device and sample syringe were rinsed out twice, between samples, with organic free water. Whenever an unusually concentrated sample was encountered, it was followed by an analysis of organic-free water to check for cross-contamination

after the system was cleaned by rinsing. For samples containing large amounts of water soluble materials, suspended solids, or high boiling compounds, it was necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a  $105^{\circ}\text{C}$  oven between analyses.

The Bellar-Lichtenburg (purge and trap) technique was used with the following conditions:

sample size
purge time
purge rate
sample purge temperature
purge gas
desorption time
desorption temperature
desorption flow rate
Cryo temperature
trap condition time
trap operating temperature
trap condition temperature

GC column (capillary)

trap support medium

10 grams
12 minutes
20 ml/minute
55°C
organic free helium
3.5 minutes
180°C
1 ml/minute
liquid nitrogen temperature
12 minutes
5°C
approximately 25°C greater than desorption temperature
DB5, 30 m. - cryogenically cooled during desorption
Tenax GC polymer (60/80 mesh) and
Silica gel

Recommended GC conditions:

Trap desorb into column/GC oven  $@25-30^{\circ}$ C GC oven isothermal  $@30^{\circ}$  C.

3.5 min. 5.5 min.

Oven temperature program sequence:

 $6^{0}/\text{min.}$  for 20 min. hold at  $150^{0}$  for 5 min.

The Bellar-Lichtenberg device was interfaced via heated transfer line to a fused silica capillary column gas chromatograph that was interfaced to the mass spectrometer via direct introduction into the ion source. The low resolution mass spectrometer was scanned from 35 to 275 amu at 1 second per decade with a minimum resolution of 600 (10% valley definition).

An INCOS computer system was interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system was also equipped with mass storage devices for saving all data from GC/MS runs. Available software allowed searching of GC/MS runs for specific ions and plotting the intensity of the ions versus time or scan number. Specific ion plot peak integration allowed for quantitation of the volatile sample components.

In order to realize the advantage of capillary columns for volatile organics analyses it was necessary that some of the column be cryogenically cooled during desorption from the Tenax trap. This was done so that desorbed compounds would be trapped in a narrow band at the head of the column prior to GC analyses. This was effectively accomplished by cooling the first coil of the column to liquid nitrogen temperature.

A GC/MS system calibration check was accomplished daily and checked every eight hours. Fifty nanograms of 4-bromofluorobenzene (BFB) was injected into the GC/MS system through the GC inlet for calibration check. A fifty nanogram sample gave ion abundances as indicated in Table 3-3.

TABLE 3-3. BFB KEY IONS AND ION ABUNDANCE CRITERIA.

<u>Mass</u>	Ion Abundance Criteria
50	20-40% of mass 95
75	50-70% of mass 95
95	base peak, 100% relative abundance 5-9% of mass 95
173 174 175 176 177	less than 1% of mass 95 70-90% of mass 95 5-9% of mass 95 70-90% of mass 95 5-9% of mass 95

All ions listed must be present in the spectrum.

A schematic of the hardware and interfacing layout used is presented in Figure 3-2.

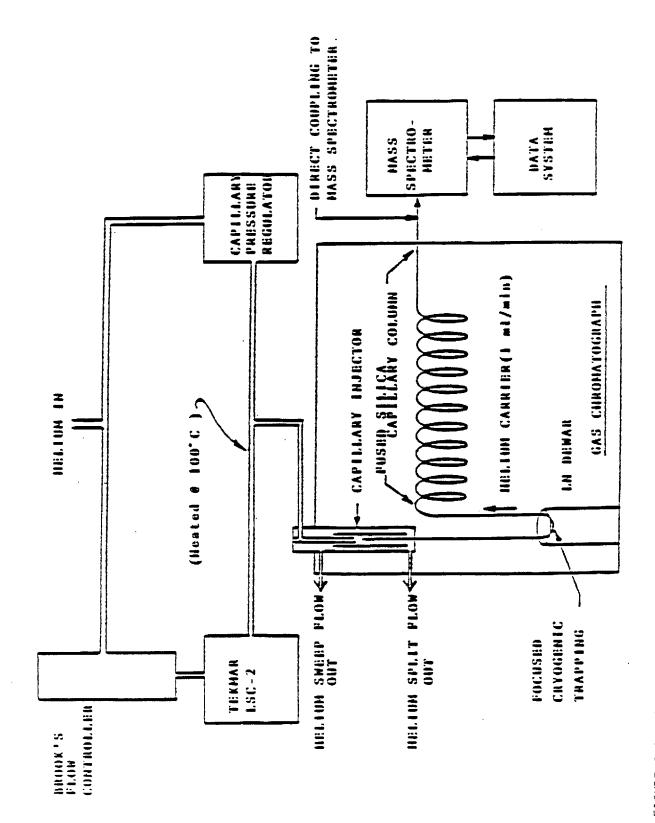
Stock standards (2 mg/ml) were prepared in methanol using assayed liquids, and mixed working standards were prepared from stock in methanol at concentrations bracketing the working range of the chromatographic system. In some cases commercially prepared stock standards (0.02 mg/ml) were used in the preparation of the working standards. Surrogate stock standards (2 mg/ml) were also prepared in methanol (D-6 Benzene, D-8 Toluene, D-10 Ethylbenzene, and D-4 1,2-Dichlorobenzene), and a surrogate standard dosing solution (20  $\mu$ g/ml) was prepared by dilution of the stock standard with organic-free water. Commercially available internal standards (0.02 mg/ml) prepared in methanol were used for spiking standards and samples just prior to the start of the purge cycle (bromochloromethane, 2-bromo-1-chloropropane, and 1, 4-dichlorobutane). Internal standards were used as an aid in quantifying compounds found (See Table 3-4) and as a check on the operation of the analytical system.

Prior to sample analysis the linear working range of the complete analytical system was checked by analyzing mixed working standards spiked into 10 ml of organic free water. A minimum of three concentrations were analyzed to insure linearity.

The tenax trap was conditioned each night at  $180^{\circ}\text{C}$  by backflushing with helium flow of 20 ml/min. Daily between each sample/standard analysis the trap was conditioned by backflushing at  $210^{\circ}\text{C}$ .

### EPA Priority Pollutant Base-Neutral, Acid Compounds, Pesticides and PCBs

Although procedures for glassware preparation vary somewhat according to the type of apparatus involved, the protocol for most apparatus involved thorough washing, solvent rinsing and high temperature oxidation. This procedure has been proven extremely effective for elimination of contamination in trace level organic analyses.



Interfacing Schematic for the Tekmar LSC-2 and 6C/MS used to Analyze Refinery Wastes for Volatile Organics. FIGURE 3-2.

TABLE 3-4. Internal Standards Used for Quantifying Volatile Organic Priority Pollutants.

## Purgable Organics

## Internal Standard For Quantitation\*

Acrolein	Bromochloromethane
Acrylonitrile	, <b>u</b>
Benzene	18
Carbon Tetrachloride	и
Chloroethane	u
2-chloroethyl vinyl ether	ii
Chloroform	u
bis(Chloromethyl)ether	u
1,1-Dichloroethane	u
1,2-Dichloroethane	ii .
1,1-Dichloroethylene	н
1,2-trans-Dichloroethylene	и
Methyl bromide	и
Methyl chloride	10
Methylene chloride	и
1,1,1-Trichloroethane	u
Vinyl chloride	II
Chlorodibromomethane	2-Bromo-1-chloropropane
Dichlorobromomethane	4
Tol uene	II
1,2-Dichloropropane	ii .
1,3-Dichloropropene	ii .
Tetrachloroethylene	10
1,1,2-Trichloroethane	-10
Trichloroethylene	10
Bromo form	1,4-Dichlorobutane
Chlorobenzene	н
Ethylbenzene	u
I,1,2,2-Tetrachloroethane	H

<sup>\*</sup>The analysis of volatile organics utilizes three internal standards for quantitation and relative retention times.

Solvent quality was also monitored and checked for contamination prior to use by concentration (volume reduction) and GC analysis. All solvents used were distilled-in-glass reagents suitable for pesticide residue analysis.

Sediment and sludge samples were prepared for priority pollutant analysis utilizing a rigorous shaker table extraction procedure. A summary of this protocol follows:

- 1) A 100 gm aliquot of sediment was transferred to a clean, tared Teflon beaker and the sample weight was accurately determined.
- 2) The sample was initially extracted with 50 ml of methanol for a 2-hour period to affect drying.
- 3) The methanol extract was decanted after centrifugation and set aside for future use.
- 4) Steps 2) and 3) were repeated and the methanol extracts were combined.
- 5) 150 ml of 35:65 methanol/methylene chloride solution were then added to the extraction vessel and the sample was agitated for a 12-hour period.
- 6) The methanol/methylene chloride extract was decanted after centrifugation and combined with the methanol.
- 7) Steps 5) and 6) were repeated with sample agitation for 6 hours.
- 8) The combined methanol/methylene chloride extract was filtered through a glass fiber filter and transferred to a separatory funnel.
- 9) 500 ml of organic-free water were added to the separatory funnel, the solution was adjusted to pH 11, and the organics were repartitioned by agitation of the separatory funnel.
- 10) At this point, the phases were separated (acid compounds were in the pH ll methanol/water phase and base-neutral/pesticide compounds were in the methylene chloride phase) by draining the methylene chloride phase through a  ${\rm Na_2SO_4}$  drying column and into a K-D flask.

- 11) The basic methanol/water phase was adjusted to pH2 and extracted 3X with methylene chloride (acid extract).
- 12) Each of the three methylene chloride extracts were drained through a  ${\rm Na}_2{\rm SO}_4$  drying column and combined in a K-D flask.
- 13) The acid fraction extracts were concentrated to a final volume of 1.0 ml and transferred to crimp-top vials for analysis.
- 14) Base-neutral/pesticide extracts were concentrated to 1.0 ml and split into two 0.5 ml fractions.
- 15) One of the 0.5 ml base-neutral/pesticide fraction extract was transferred to crimp-top vial for pesticide analysis by gas chromatography with electron capture detection (GC/ECD).

Semi-aqueous samples were prepared for priority pollutant analysis using EPA methods 608 and 625 as described in the December 3, 1979 Federal Register.

The GC/MS analyses of base-neutral and acid extracts were carried out using a 30 m. x 0.32 mm i.d. DB5 fused silica capillary column directly coupled to the mass spectrometer ion source. One microliter of extract was injected splitless with inlet purge after 30-40 seconds. Helium carrier gas flow velocity was 40-45 cm/sec. Column oven temperature was programmed from  $30^{\circ}\text{C}$  to  $275^{\circ}\text{C}$  at  $3.5^{\circ}\text{C/min}$ . The mass spectrometer was scanned over the mass range of 34-475 at a rate of 1 second per decade. Data files of 4000 spectra were typically acquired for each sample extract analysis.

Decafluorotriphenyl phosphine (DFTPP) was injected daily to monitor ion abundance. Table 3-5 lists the DFTPP key ions and ion abundance criteria.

Just prior to GC/MS analysis of the various fractions of the semi-volatiles (acid, base and neutrals) a known amount (20 g) of decadeutero-phenanthrene was added to the concentrated extracts as an internal standard.

TABLE 3-5. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68 70	less than 2% of mass 69 less than 2% of mass 69
127	40-60% of mass 198
197 198 199	less than 1% of mass 198 base peak, 100% relative abundance 5-9% of mass 198
275	10-30% of mass 198
365	greater than 1% of mass 198
441 442 443	less than mass 443 greater than 40% of mass 198 17-23% of mass 442

All ions listed must be present in the spectrum.

EPA designated priority pollutants (see Table 3-6) were determined and quantified by manually plotting three overlapping selected ion records for each compound. The selected groups of ions used are listed in Tables 3-7 and 3-8.

Compound identification was confirmed when the retention time at the experimental mass spectrum was within  $\pm$  15 seconds of the retention time of the authentic compound or  $\pm$ .02 relative retention to the d<sub>10</sub>-Phenanthrene internal standard, whichever was greater.

Prior to sample analysis a three point calibration curve was generated for each of the compounds listed in Table 3-6. Mixed working standards used to generate the calibration curve were prepared from commercially available stock standards of the individual compounds in methanol.

#### Petroleum Hydrocarbons

The base-neutral extracts prepared as described in the preceding section were analyzed for petroleum hydrocarbons by gas chromatography with flame ionization detection (GC/FID). The analyses were performed using a 30 m x 0.32 mm i.d. DB5 fused silica capillary column. One microliter of extract was injected splitless with inlet purge after 60 seconds. The column inlet pressure was maintained at 10 psi helium. The column oven temperature was programmed from  $45^{\circ}$ C (held 5 min initially) to  $280^{\circ}$ C at  $3.5^{\circ}$ C/min. Hydrogen flow to the detector was 30 ml/min, and air flow to the detector was 240 ml/min.

The gas chromatograph was calibrated daily or after every ten injections during 24 hour/day operation using a series of even and odd n-alkanes from nC-8 through nC-32. A stock standard was prepared in hexane at a concentration of 250  $\mu g/ml$  of each n-alkane from nC-8 through nC-32. The stock standard was prepared from the neat compounds. A working standard at 25  $\mu g/ml$  was prepared from the stock solution.

#### TABLE 3-6. EPA Designated Priority Pollutants Compounds.

#### Semivolatile (Extractable) Organics:

Acenaphthene

Acenaphthylene

Anthracene

Benzidine

Benzo (a) anthracene

Benzo (b) fluoranthene

Benzo (g,h,i) perylene

Benzo (a) pyrene

4-Bromophenyl phenyl ether

Butyl benzyl phthalate

p-Chloro-m-cresol

bis (2-Chloroethoxy) methane

bis (2-Chloroethyl) ether

bis (2-Chloroisopropyl) ether

2-Chloronaphthalene

2-Chlorophenol

4-Chlorophenyl phenyl ether

Chrysene

Dibenzo (a,h) anthracene

Di-n-butyl phthalate

Dichlorobenzenes (3 isomers)

3,3'-Dichlorobenzidine

2,4-Dichlorophenol

Diethyl phthalate

2,4-Dimethylphenol

Dimethyl phthalate

4,6-Dinitro-o-cresol

2,4-Dinitrophenol

2,4-Dinitrotoluene

2,6-Dinitrotoluene

Di-n-octyl phthalate

1,2-Diphenylhydrazine

bis (2-Ethylhexyl) phthalate

Fluoranthene

Fluorene

Hexachlorobenzene

Hexachlorobutadiene

Hexachlorocyclopentadiene

Hexachlorocyclopentadiene

Hexachloroethane

Indeno (1,2,3-c, d) pyrene

Isophrone

Naphthalene

Nitrobenzene

2-Nitrophenol

4-Nitrophenol

N-Nitrosodimethylamine

N-Nitrosodiphenylamine

N-Nitrosodi-n-propylamine

Phenanthrene

Pheno1

Pentachlorophenol

Pyrene

1,2,4-Trichlorobenzene

2,4,6-Trichloro phenol

TABLE 3-7. Base/Neutral Extractables Characteristic Ions.

	Characteristic Ions Electron Impact		
Compound			
1,3-Dichlorobenzene	146	140	
1,4-Dichlorobenzene	146	148	113
Hexachloroethane	、146 117	148	113
Bis (2-chloroethyl) ether	117	201	199
1,2-Dichlorobenzene	93	63	95
Bis (methyl-2-chloroethyl) ether	146	158	113
N-Nitrosodipropyl amine	45	77	79
Isophorone	130	42	101
Nitrobenzene	82	95	138
Hexachlorobutadiene	77	123	. 65
$\cdot$	225	223	227
1,2,4-Trichlorobenzene	180	182	109
Naphthalene	128	129	127
Bis (2-chloroethoxyl) methane	93	95	123
Hexachlorocyclopentadiene	237	235	272
Acenaphthylene	152	151	153
Acennaphthene	154	153	152
Dimethyl phthalate	163	194	164
2,6-Dinitrotoluene	165	63	121
Fluorene	166	165	167
4-Chlorophenyl phenyl ether	204	206	141
2,4-Dinitrotoluene	165	63	182
1,2-Diphenylhydrazine*	77	93	105
N-Nitrosodiphenylamine**	169	168	167
Hexachlorobenzene	284	142	249
4-Bromophenyl phenyl ether	248	250	141

<sup>\*</sup>Detected as azobenzene \*\*Detected as diphenylamine

TABLE 3-7. Base/Neutral Extractables Characteristic Ions. (Continued)

	Characteristic Ions		
Compound	Electron Impact		
Phenanthrene	178	179 17	6
Anthracene	178	179 17	6
Dibutyl phthalate	149	150 10	14
Fluoranthene .	202	101 10	0
Ругеле	202	101 10	0
Benzidine	184	92 18	5
Bis(2-ethyl hexyl) phthalate	149	167 27	9
Chrysene	228	226 22	9
Benzo (a) anthracene	228	229 22	6
3,3'-dichlorobenzidine	252	254 12	6
Dioctyl phthalate	149		
Benzo (b) fluoranthene	252	253 12	:5
Benzo (a) pyrene	252	253 12	:5
Indeno (1,2,4-c,d) pyrene	276	138 27	7
Dibenzo (a,h) anthracene	278	139 27	9
Benzo (g,h,i) perylene	276	138 27	7
N-nitrosodimethyl amine	42	74 4	4
Bis (chloromethyl) ether	45	49 5	1
2,3,7,8-Tetrachlorodibenzo-p-dioxin	322	320 5	9
Deuterated phenanthrene (d-10)	188	94 8	0

TABLE 3-8. Acid Extractable Characteristic Ions

Compound		cteristic ectron Impa	
2-Chlorophenol	128	64	130
2-Nitrophenol	139	65	109
Phenol	94	65	66
2,4-Dimethylphenol	122	107	121
2,4-Dichlorophenol	162	164	98
2,4,6-Trichlorophenol	196	198	200
4-Chloro-3-methyl phenol	142	107	144
2,4-Dinitrophenol	184	63	154
2-Methyl-4,6-dinitrophenol	198	182	77
Pentachlorophenol	266	264	268
4-Nitrophenol	65	139	109
Phenanthrene (d-10)	188	94	80

The GC/FID analyses were completed on a Hewlett Packard 5840A gas chromatograph which was interfaced to a Texas Instruments Silent 700 ASR electronic data terminal. In this manner all digital chromatographic data were recorded on magnetic tape for computerized data reduction and analysis. With this system the following information is available: total mass of resolved hydrocarbons, total mass of unresolved hydrocarbons, mass of n-alkanes, mass of even n-alkanes, mass of odd n-alkanes, and the ratios pristane/nC-17, phytane/ nC-18, and pristane/phytane. In addition, compound specific concentrations are computed and organized by Kovat retention indices.

#### 3.2 RESULTS AND DISCUSSION

This section of the report summarizes the results of analyses of the nine refinery waste samples collected from three California refineries: Union Oil--Rodeo, Chevron--Richmond, and Chevron--El Segundo.

#### 3.2.1 <u>Description of the Samples</u>

A total of nine refinery waste samples were characterized by the methods outlined in Section 3.1 of this chapter. Biosludge, API separator sludge, and dissolved air flotation (DAF) sludge were collected from the Union Oil Refinery located in Rodeo, California. Oil contaminated algae skimmings, oil contaminated soils from the Hazardous Waste Storage Area (HWSA) and from the San Pablo Tank Farm (SP Tank Farm), and a tank bottoms sample were collected and analyzed from the Chevron Refinery located in Richmond, California. The samples collected and analyzed from the Chevron Refinery located in El Segundo, California included induced air flotation (IAF) sludge and DAF sludge. This section of the report will describe these samples.

#### Union Oil--Rodeo

Union Oil began landfarming in 1975 with an initial acreage of 3.4 acres. As of January 14, 1983 Union Oil ceased to apply any wastes to their

landfarm. At that time the landfarm had expanded to 6.4 acres. Union Uil's moratorium on landfarming will continue until they determine what facility improvements are necessary to satisfy Regional Water Quality Control Board requirements. In 1982 Union Oil applied a total of 882,000 gallons of waste to their landfarm. The volumes of API Separator Sludge and Air Flotation Sludge applied in 1982 were approximately 54,600 and 176,400 gallons, respectively. Tank bottoms accounted for 126,000 to 336,000 gallons of waste during 1982. Other wastes applied to the landfarm during 1982 were primarily sludge from storm basin cleaning and sediments removed from sumps.

Biosludge, which originates from activated sludge from refinery wastewater treatment, is another of the waste types which is landfarmed at Union Oil. Prior to applying this waste type to the landfarm, it is transferred to one of ten open ponds which are lined with sand. The water which is inherent in the sludge is allowed to drain through the sand, and the remaining sludge is allowed to weather and dry prior to removing it and applying it to the landfarm. The sample of Biosludge which SAI collected came from four of these holding ponds. Each of the ponds had sludge which was at varying stages of weathering. The sludge from the four ponds sampled was composited so the sample represents sludge which might emit various amounts of volatile components due to the various stages of weathering.

API Separator Sludge is produced in the initial recovery of oily materials from liquids and wastewaters that are collected from various processes throughout the refinery. The oily waste is skimmed from the liquid wastes by an API Separator. This waste was sampled from the separator over a period of approximately 30 minutes as the sludge became available through the skimming process. The sample was composited before splits were taken for analysis. In 1982 this waste type accounted for about 6% of the total waste applied to the Union Oil landfarm.

DAF sludge originates from the recovery of oils from refinery waste treatment. The unit which separates oils from wastewater uses compressed air

which is injected into the waste stream. The fine air bubbles which form rise to the surface, and suspended solids or oils attach to the rising gas. A floating sludge layer is formed on the surface, and it is then mechanically skimmed to a sump. A composite sample of this sludge mixed with wastewater was collected from the sump and used for characterization. In 1982 Air Flotation Sludge accounted for approximately 20% of the total waste applied to the Union Oil landfarm.

#### Chevron--Richmond

The Chevron Refinery at Richmond, CA has been landfarming since 1975. During that time period the landfarm has expanded from less than eight acres to its present day size of 29 acres. In 1982 Chevron treated 6,636,000 gallons of waste using on-site landfarming. The major wastes and the quantities disposed of in 1982 through this technique include: oil contaminated soil and mud (4,700,000 gallons); tank bottoms (1,512,000 gallons); algae and water from the water effluent treatment system (with residual oil) (205,800 gallons); others (218,400 gallons).

Algae Skimmings mixed with residual oil originate from the refinery's water effluent treatment system. The algae waste is stored in two containers, called "Baker Boxes", each having an approximate capacity of 1000 gallons. The waste is applied directly to the landfarm from the storage containers. In 1982 this waste type accounted for about 4% of the total waste applied to the landfarm. A sample of this waste was obtained from a drain tube located at the bottom of one of the "Baker Boxes".

Two samples of oil contaminated soil were obtained from the Chevron, Richmond Refinery. The first soil was from an excavation site and was being stored at the facility's Hazardous Waste Storage Area (HWSA). The soil had been contaminated with lube oil. Although the soil appeared to be low in oil content, a sample was obtained and analyzed because Chevron is handling this soil as though it were a hazardous waste. The second soil sample came from

the San Pablo Tank Farm (SP Tank Farm), which is located approximately five miles from the Richmond Refinery. The tank farm is a storage area for crude oil that is transferred via pipeline to the Richmond facility from the San Joaquin Valley. Over the years, spillage from handling has contaminated the soil around the storage tanks and prompted Chevron to remove these materials and apply them to their landfarm. Soil scrappings were taken from about five locations which had oil spilled on them some time in the past. The scrappings were composited into one sample and were analyzed. In 1982 oil contaminated soils accounted for about 71% of the total waste applied to the Chevron landfarm in Richmond.

The fourth sample obtained from the Chevron, Richmond Refinery was a Tank Bottoms sample which was collected by Chevron Refinery personnel. The schedule for tank openings prevented SAI field sampling personnel from collecting the sample. The sample was from tank T-290 which contained "Bunker" Fuel Oil. In 1982 Tank Bottoms accounted for about 23% of the total waste applied to the landfarm.

#### Chevron--El Segundo

Landfarming at the Chevron Refinery in El Segundo began in October 1979 in an initial lot of six acres since expanded to 12 acres. In 1981 a total of 2,416,000 gallons of waste were treated through the landfarm. The major wastes and the amounts disposed of in 1981 through this technique include: Air Flotation Sludge (1,075,000 gallons); Slop Oil Emulsions (537,600 gallons); Tank Bottoms (436,800 gallons); others (366,700 gallons).

Two types of Air Flotation Sludge were collected from the Chevron Refinery in El Segundo. The first, Dissolved Air Flotation (DAF) Sludge is produced by the recovery of liquids from oily drains that originate primarily from refinery desalters. An API separator is used for the initial recovery process, and the oily materials from this separation are then treated with a polymer and placed in the DAF system. The DAF uses compressed air to agitate

and separate the oily materials from water and solids. The sludge that results from the DAF system is pumped into vacuum trucks and is either applied directly to the landfarm or placed in storage tanks. The sample of DAF Sludge which SAI obtained was from the drain line used to transfer sludge from the DAF unit to the vacuum truck. In 1981 Air Flotation Sludge accounted for 44% of the total waste applied to the El Segundo Refinery landfarm.

The second Air Flotation Sludge, Induced Air Flotation (IAF) Sludge, results from liquids that are collected from storm drains and cooling tower blow-downs. As with the DAF system an API separator is used for the initial recovery process, and then a polymer is added to promote the oil/water separation. The IAF unit employs mechanically induced air flotation to separate oils from water. The oils are recovered with a skimmer. The sludge that settles to the bottom of the tank is periodically pumped into a tank truck and either applied to the landfarm directly or placed in a storage tank to await landfarming. The sample of IAF sludge which SAI obtained was from the landfarm storage tank and contained IAF Sludge, DAF Sludge, and Slop Uil Emulsions.

#### 3.2.2 Oil and Grease

The results of analyses of refinery waste samples for 0il and 6rease are presented in Table 3-9. The samples with the highest oil and grease content are the Tank Bottoms (49%) followed by the API Separator Sludge (37%). This coincides with the physical nature of these two samples, both of which were oily in appearance. The remaining samples contain between 2 and 9 percent oil and grease except for the Algae Skimmings and the Soil from the Hazardous Waste Storage Area. These two samples showed less than a percent oil and grease.

TABLE 3-9. OIL AND GREASE IN REFINERY WASTES.

Sample Description	Oil and Grease (Wt. Percent)
Union OilRodeo Biosludge API Separator Sludge DAF Sludge	2.4 37 2.1
ChevronRichmond Algae Skimmings SoilHWSA SoilSP Tank Farm T-290 Tank Bottoms	0.03 0.20 9.0 49
ChevronEl Segundo DAF Sludge IAF Sludge	6.5 6.5

#### 3.2.3 Total Suspended Solids and Total Dissolved Solids

The results of analyses of refinery waste samples for Total Suspended Solids (TSS) and Total Dissolved Solids (TDS) appear in Table 3-10. The results are expressed in mg/ml for the aqueous samples while the results for sludges and soils which were suspended in water are expressed in mg/g of wet sample. The samples with the highest TSS levels are the soils and sludges. The TSS levels for the aqueous samples are considerably lower. The same trend applies to the data for TDS. However the differences between the the aqueous samples and the soil sludges is not as great as for TSS with the exception of the Algae Skimmings sample from Chevron--Richmond the (TDS value for this sample was lower than those of the remaining samples by greater than an order of magnitude).

#### 3.2.4 Percent Moisture

The results of analyses of refinery waste samples for their moisture content appear in Table 3-11. The results reflect the differences between the two analytical procedures, heating the sample at  $100^{\circ}$ C to a constant weight, and freeze drying the sample. The results using the heating method are lower than or equal to those using the freeze drying method in all cases.

The actual percent moisture is probably closer to the heating method value due to an apparent lose of volatile material other than water from the sample during the freeze drying process.

All of the samples are high in water content with the exception of the soils and tank bottom sample. DAF and IAF sludge samples are a combination of oil, grease, and solids removed from refinery wastewater. During the separation of the oil from the aqueous phase by skimming, water is also entrained. Therefore in sampling these sludges a large amount of water is present. The algae skimmings also resulted from wastewater treatment, and thus, they had a high percentage of water. Although the biosludge was

TABLE 3-10. TOTAL SUSPENDED SOLIDS (TSS) AND TOTAL DISSOLVED SOLIDS (TDS) IN REFINERY WASTES.

	<u>TS</u>	<u>ss</u>	<u>Tt</u>	<u>)S</u>
Sample Description	<u>(mg/g)</u>	<u>(mg/ml)</u>	<u>(mg/g)</u>	(mg/ml)
Union OilRodeo				
Biosludge API Separator Sludge DAF Sludge	240 250 	  29	8.2 30 	1.9
ChevronRichmond				
Algae Skimmings SoilHWSA SoilSP Tank Farm T-290 Tank Bottoms	840 760 NA	56   	23 6.7 NA	0.05   
ChevronEl Segundo				
DAF Sludge IAF Sludge	120	78 	 17	6.7

NA = Not Analyzed

Sample T-290 Tank Bottoms was not analyzed because it was insoluble in water.

TABLE 3-11. PERCENT MOISTURE OF REFINERY WASTES.

Wt. Percent Moisture

Sample Description	Heating	Freeze Drying*
Union OilRodeo		
Biosludge API Separator Sludge DAF Sludge	60 39 84	77 47 94
ChevronRichmond		
Algae Skimmings SoilHWSA SoilSP Tank Farm T-290 Tank Bottoms	84 9 13 17	98 12 13 19
ChevronEl Segundo		
DAF Sludge IAF Sludge	80 69	89 79

<sup>\*</sup>May include some volatile material other than water.

composited from sludge at various stages of weathering, there was still sufficient water present to yield a relatively high percentage of moisture.

#### 3.2.5 Heat of Combustion

Heats of combustion for the nine refinery waste samples are listed in Table 3-12. The heat of combustion of a material is the quantity of energy or heat that is generated by the complete combustion of a unit weight of the material. The sample with the highest heat of combustion is the Tank Bottoms. The API Separator Sludge and the two DAF Sludge samples also had relatively high heats of combustion. These results are not surprising as one would expect high heats of combustion for samples that are oily in nature. The relatively high heat of combustion for the San Pablo Tank Farm Soil indicates that it had a considerably higher degree of oil contamination than did the Soil which was sampled from the Hazardous Waste Storage Area. This is consistent with the Oil and Grease results listed in Table 3-9 and with results generated by GC-FID and GC/MS analysis as described in Sections 3.2.7 through 3.2.9. The heat of combustion for the IAF Sludge from Chevron -- El Segundo is lower than expected based on the Oil and Grease results listed in Table 3-9.

#### 3.2.6 EPA Priority Pollutant Trace Metals

The analyses of refinery waste samples for trace metals yield data which can be used to predict the potential for contamination of landfarm soils. The metals burden of these samples would not be expected to produce unusual volatile emissions except where samples showed elevated levels of mercury.

The results of analyses of the waste samples for the 13 priority pollutant trace metals appear in Table 3-13. Also included in Table 3-13 are average earth crustal abundances for these metals. When compared to the average crustal abundances, several of the waste samples show elevated levels of

#### TABLE 3-12. HEAT OF COMBUSTION OF REFINERY WASTES.

#### Heat of

	Heat of
Sample Description	Combustion (BTU/1b)
Union UilRodeo	
Bi osludge	28
•	
API Separator Sludge	5130
DAF Sudge	5420
	•
ChevronRichmond	
03 Chii	204
Algae Skimmings	
SoilHWSA	32
SoilSP Tank Farm	2760
T-290 Tank Bottoms	13200
ChevronEl Segundo	
DAC Cludge	<b>L600</b>
DAF Sludge	5690
IAF Sludge	69

TABLE 3-13. TRACE METALS IN REFINERY WASTES, CONCENTRATIONS IN µg/g DRY WEIGHT.

Sample Description	qs	As	Be	P3	ئ	r <sub>O</sub>	HA.	H	i i	3		ļ	
Inion Dil Dodos										אַל	Đ.	=	u7
Biosludge	⊽	16	0.37	1.2	360	44	69	4.4	38	260	0.48	<0.2	470
API Separator Sludge	1.5	9.2	0.29	7.4	420	160	440	110	190	210	0.46	<0.1	390
DAF Sludge	1.3	44	0.63	2.7	1500	87	240	4.8	53	110	0.75	<0.1	940
Chevron - Richmond Algae Skinmings	7	56	0.80	2.2	780	790	190	4.2	2100	7.1	0.98	<0.2	520
Soil - HWSA	100	21	0.82	0.50	27	130	1100	0.24	130	33	0.23	<0.1	750
Soil - SP Tank farm	<0.6	09	0.54	0.37	24	13	150	0.20	24	34	0.10	<0.1	18
T-290 Tank Bottoms	1.2	14	0.26	0.56	53	130	140	1.3	190	21	0.27	<0.05	920
Chevron - El Segundo DAF Sludge	<0.8	71	0.21	5.0	200	230	170	7.6	28	06	0.21	<0.2	2100
IAF Sludge	4.8	28	0.49	48	2400	770	890	17	200	64	1.2	<0.1	8000
Average Earth's Crust	_	5	9	0.15	200	70	91	0.5	08	1:1	0.1	9.0	130
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												· ·	

the metals which indicates the potential for metals buildup in the soils of the landfarms. This potential buildup of metals is particularly apparent for Cd, Cr, Cu Pb. Hg, Se, and Zn.

The two soil samples analyzed from the Chevron Refinery at Richmond might be expected to give an indication of the trace metal levels of ambient soils in that area. However, it appears that the soil from the Hazardous Waste Storage Area has elevated levels of Sb Cu Pb Ni and Zn relative to the SP Tank Farm soil. The concentrations of the remaining metals are similar between the two samples Compared to the crustal abundances however the two soil samples also show high levels of As and Se. Therefore, it is difficult to ascertain the background soil concentrations of these metals.

The samples which appear to have the greatest potential for contributing to buildup of metals in the soils of landfarms are DAF and IAF Sludges and Algae Skimmings. The DAF and IAF Sludges are particularly elevated in Cd. Cr., Pb. Se and Zn especially when compared to the average crustal abundances for these metals. The Algae Skimmings were high in Cr., Cu., Pb., Ni and Se. The remaining samples show high levels for some of the metals also but the overall potential for metals buildup appears to be greatest for the above three sample types.

## 3.2.7 EPA Priority Pollutant Volatile Organics in Petroleum Landfarm Waste Samples

As noted earlier, a potential source of volatile organic compounds causing air pollution problems may result from landfarming operations involving various oil refinery sludges. In an attempt to evaluate this potential source of volatile organic air pollutants the nine aforementioned sludge wastes were subjected to chemical analysis for EPA Priority Pollutant Volatile Organics

This section presents the results of EPA Priority Pollutant Volatile Organics analyses as completed by purge and trap GC/MS. Section 3.2.8 presents the results of total hydrocarbons as determined by GC-FID and Section 3.2.9 presents the results of EPA priority pollutant semi-volatile organics as determined by liquid extraction and GC-FID and GC/MS analysis. Complete details for the methodology involved for the purge and trap GC/MS analyses and the liquid-liquid hydrocarbon and semi-volatile organics analyses are presented in Section 3.1.2. In addition, to evaluate the Suggested Control Measure (gravimetric purge and trap screening procedure) proposed by CARB, six selected sludge samples were subjected to Suggested Control Measure procedure for comparison of results between SAI and CARB. These data are presented in a separate Appendix.

Table 3-14 lists the concentrations of EPA priority pollutant volatile organics found in the refinery waste and sludge samples. The priority pollutant concentrations are in (nanogram or  $10^{-9}$ ) ng/g of wet sample as determined by purge and trap GC/MS analysis of the samples as received from the refineries. The "Total Concentrations of Volatiles" are in  $\mu g/g$  wet sample, and these values were obtained by applying average response factors for five volatile priority pollutants (benzene, toluene, ethylbenzene, m.p-xylene, o-xylene) eluting throughout the molecular weight range of interest to the total area under <u>all</u> the integrated peaks observed in each sample.

As the data illustrate, fairly low individual levels of priority pollutant volatile organics are found with the range going from below the detection limit of 1 ng/g to upwards of 9,500 ng/g in the various refinery wastes considered. Clearly, there are significant differences in comparing the different waste types, and clear trends are observed for the group of five priority pollutant organics considered among the soil and sludge samples. These relative trends are also reflected in the total mass of volatiles obtained from summing all of the integrated peaks in each sample.

EPA PRIORITY POLLUTANT VOLATILE ORGANICS IN REFINERY WASTES. CONCENTRATIONS ARE IN ng/g OF WET SAMPLE EXCEPT WHERE INDICATED. **TABLE 3-14** 

Sample Description	Benzene	Toluene	Ethyl Benzene	M,P-Xylene	0-Xylene	Chloroethane	1,1-dichloro- ethane	lotal concentration <sup>2</sup> (ug/g)
	Al	83	C	O	ш	9	=	
Union Oil - Rodeo								
Biosludge	54	810	92	570	240	ON	0.63	23
API Separator Sludge	820	840	310	820	089	QN	Q.	180
DAF Sludge	1800	1600	160	099	240	QN	51	160
Chevron - Richmond								
Algae Skimmings	160	570	300	260	320	32	4.4	130
Soil - HWSA	1.8	QN	QN	QN	S.	QN	QV	0.4
Soil - SP Tank Farm	46	1100	9/	720	300	QN	1.7	16
T-290 Tank Bottoms	170	1500	280	610	300	QN	22	95
Chevron - El Segundo								
DAF Sludge	9200	1500	180	570	280	ND	QN	110
IAF Sludge	1700	640	220	720	330	95	510	110

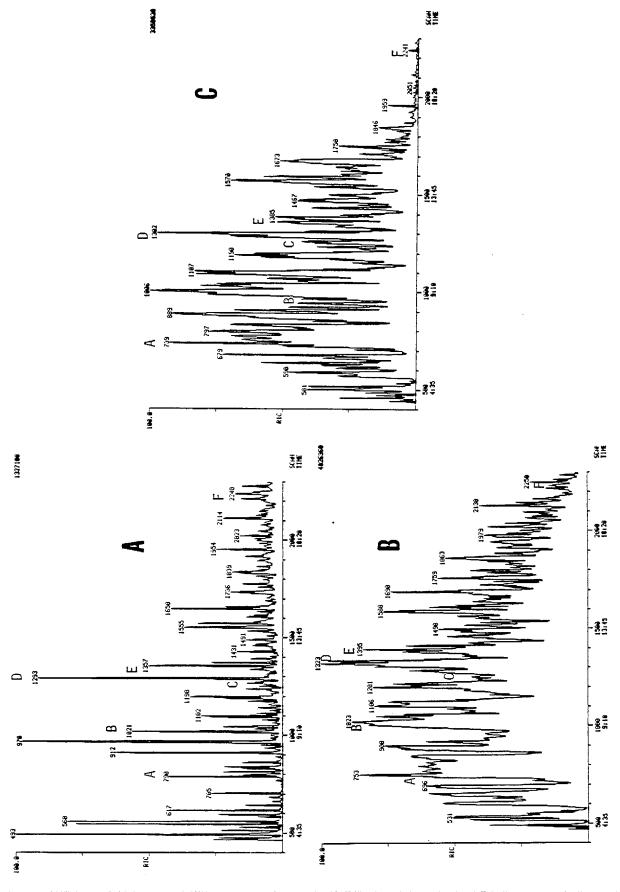
1. Letters represent components peaks labelled in Figures 3-3 through 3-5.

Total concentration of volatiles was calculated from the average response factors for Benzene, Toluene, M.P-Xylene and O-Xylene based on the total area of the reconstructed ion chromatograms of both identified and unidentified peaks. These four peaks were used since they are most representative compounds of the volatile components of the sample. 2,

#### Union Oil -- Rodeo

Figure 3-3 presents the reconstructed ion chromatograms obtained on the three sludge samples obtained from Union Oil-Rodeo. Figure 3-3A is the chromatogram from the biosludge; 3-3B is the chromatogram from the API separator sludge; and 3-3C is the chromatogram from the DAF sludge. Clearly from the results presented in Table 3-14 and the chromatograms in Figure 3-3, it can be seen that the biosludge has the lowest overall concentration of volatile organics and specific EPA priority pollutant compounds. This is reflected by the lack of complexity in the chromatographic profile in Figure 3-3A compared to Figures 3-3B and 3-3C and by the quantitative data presented in the Table. The letter-labelled peaks in the reconstructed ion chromatograms are the single identified priority pollutant organics listed in Table 3-14. chromatograms demonstrate that the five aromatic priority pollutants are present in all three samples, but the API separator sludge and DAF sludge are clearly more contaminated as numerous other components are present as well. By summing the mass of these other components in addition to the five priority pollutant organics listed in Table 3-14, the total mass of volatiles in the biosludge is observed to be only 23  $\mu$ g/g compared to 180  $\mu$ g/g and 160  $\mu$ g/g for the API separator sludge and DAF sludge, respectively. Thus, it appears that the biodegradation or preweathering treatment employed before landfarming significantly removes many of the lower molecular weight components. Their introduction into the air should thus be a consideration during this preweathering stage more than during ultimate landfarming of this material.

Interestingly, the chromatographic profiles obtained on the API separator sludge and the DAF sludge are very similar, with order of magnitude higher levels of individual components being noted in these samples, compared to the biodegraded sludge.



Reconstructed Ion Chromatograms Obtained From GC/MS Volatile Organic Analyses of Union Oil, Rodeo Refinery Sludge Samples: A) Biosludge; B) API Separator Sludge; and C) DAF Sludge. Identification of Letter Labelled Peaks are in Table 3-14 except F-Napthalene shown in Table 3-16. Time from point 0.0 when identification \*RIC - Reconstructed Ion Chromatograph \*\*Scan number of cycles scanned at certain point in the analysis. FISURE 3-3.

is made in the analysis.

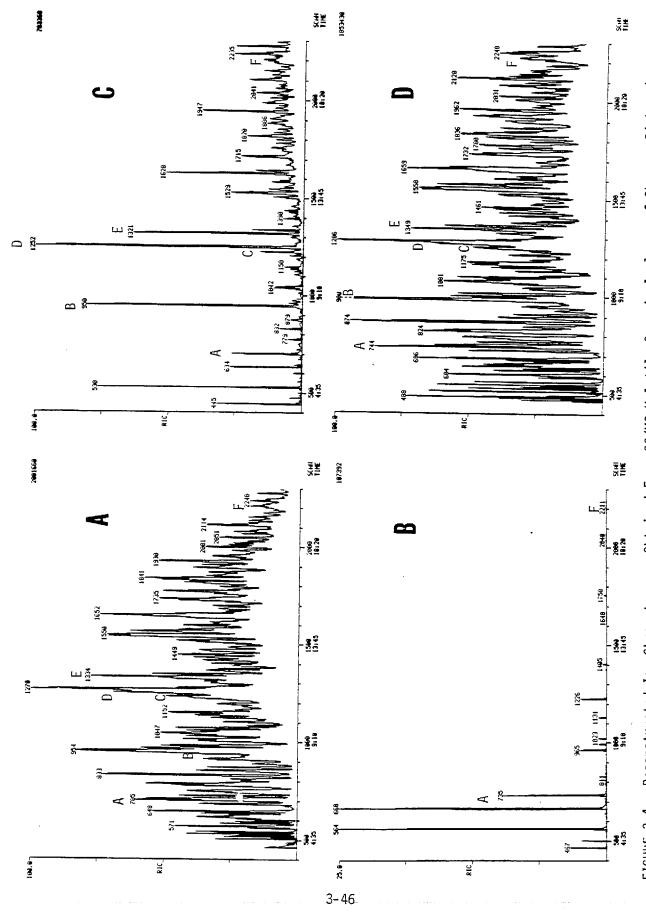
3-44

#### Chevron -- Richmond

Figure 3-4 presents the volatile organic analysis results obtained on the four samples collected from the Chevron, Richmond Refinery. Figure 3-4A is the volatile components present in the aqueous/sludge sample obtained from the algae skimmings drum. In that sample there is significant evidence of lower molecular weight aromatics present in addition to other unresolved and unidentified volatile components. This is reflected in the complexity of the chromatogram in Figure 3-4A, as well as in the quantitative data presented in Table 3-14. Interestingly, the Total Mass of Volatiles in this sample is only slightly lower than those observed in the API and DAF sludge from the Union Oil - Rodeo Refinery.

The chromatograms shown in Figures 3-4B and 3-4C were generated from the Hazardous Waste Storage Area soil and the the San Pablo Tank Farm soil, respectively. The Hazardous Waste Storage Area soil sample represented a sample which was to have been landfarmed at a later date, and quite surprisingly, there are very few volatile components remaining in this soil. As will be noted in the next section, this sample also contained the lowest overall petroleum hydrocarbon contamination of all of the samples analyzed. In fact, benzene was only detected at a level of 1 ng/g of wet sample, and none of the other EPA priority pollutants were observed.

The soil sample from the San Pablo tank farm in Figure 3-4C did show somewhat greater complexity compared to the other soil, and the overall levels of individual EPA priority pollutant volatile organics were similar to those observed in the algae skimmings sample from this refinery. The total mass of volatiles in the SP tank farm soil, however, was significantly less than the total mass of volatile from the algae skimmings. Nevertheless, there were more volatile components present in the soil around the tank farm, compared to the "Hazardous Waste Storage Area" sample. These components presumably reflect materials introduced during slight spills of refined or crude petroleum products during tank fillings and discharges.



Reconstructed Ion Chromatograms Obtained From GC/MS Volatile Organic Analyses of Chevron Richmond Refinery Samples: A) Algae Skimmings; B) Soil From Hazardous Waste Storage Area; C) Soil From San Pablo Tank Farm; and D) T-290 Tank Bottoms. Identification of Letter Labeled Peaks are in Table 3-14. FIGURE 3-4.

Figure 3-4D presents the chromatogram obtained from GC/MS Volatile Organic Analyses of the Richmond Refinery tank bottoms sample obtained for SAI by Chevron personnel. (As noted in the introduction to this chapter, all samples were obtained on an "as available or opportunistic basis" and during our initial visit to this site, we were unable to obtain a sample from tank T290.) Clearly, the VOA profile of this sample is more complex than any other obtained from the Chevron, Richmond Refinery, and the total EPA priority pollutant volatile organic concentrations are in line with the levels of these components in the algal skimmings discharge tank. The two profiles are quite similar in overall complexity, and as the "Letter-labeled" peaks in both chromatograms illustrate that common levels of priority pollutant organics are observed.

#### Chevron -- El Segundo

Figure 3-5 presents the reconstructed ion chromatograms obtained from the GC/MS Volatile Organic Analyses of the two sludge samples obtained from the Chevron Refinery at El Segundo. Figure 3-5A is the chromatogram obtained from the DAF sludge sample and Figure 3-5B is the chromatogram obtained from the IAF sludge sample. Interestingly, the profiles are nearly identical, and they are very similar in appearance to the Union Oil Refinery API volatile and DAF volatile organic samples shown in Figure 3-3B and 3-3C. Note also that the Total Mass of Volatiles in the El Segundo samples are only slightly less than those from Union Uil - Rodeo. Clearly this reflects the similarity of the materials present in common waste streams and the fact that the various separator techniques were used in conjunction with sludge treatment. overall concentrations of EPA priority pollutant volatile organics in the El Segundo samples are similar to those observed in the API separator sludge and DAF separator sludge, with the exception that the benzene level in the Chevron, El Segundo DAF sludge is significantly higher than any other benzene level measured during volatile organics analysis.

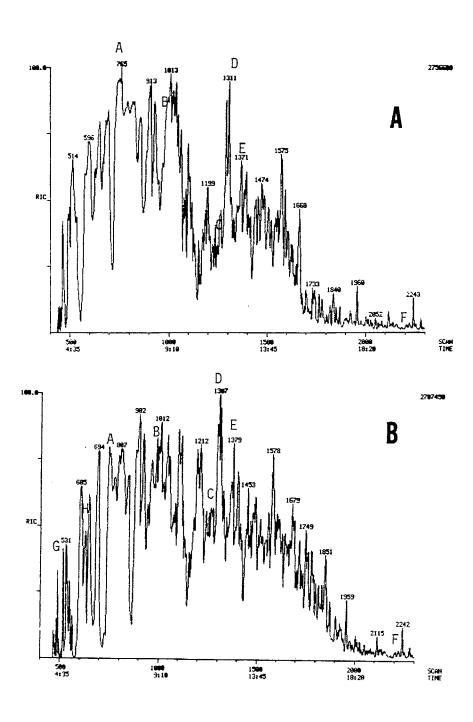


FIGURE 3-5. Reconstructed Ion Chromatograms Obtained From GC/MS Volatile Organic Analyses of Chevron, EL Segundo Refinery Samples: A) DAF Sludge; and B) IAF Sludge. Identification of Letter Labelled Peaks are in Table 3-14.

From those results, it is clear that the soil samples obtained around the San Pablo Tank Farm and the soil sample designated for Hazardous Waste Disposal showed the lowest levels of volatile organics. The liquid sludge samples from the DAF and IAF treatments showed the highest levels of volatile organics, and the biosludge from Union Oil (where the sample was preweathered) had levels intermediate between those for the API separator sludge and the soil samples examined from Richmond Refinery. Also, samples with higher percent moisture levels (see Table 3-11) generally had higher total levels of volatiles.

#### 3.2.8 Results of Intermediate and Higher Molecular Weight Petroleum Hydrocarbon and EPA Priority Pollutant Semi-Volatile Organic Analyses in Refinery Wastes

Table 3-15 presents the results of petroleum hydrocarbon determinations in the refinery wastes, as measured by flame ionization detector gas chromatography. Comparison of the total resolved hydrocarbon concentrations and total hydrocarbons present in the Unresolved Complex Mixtures (UCM) of the chromatographic profiles obtained on the samples shows a trend which parallels the total concentration of volatile organics for some of the refinery wastes. For example, this trend is followed closely for all samples from Chevron, Richmond except for the Algae Skimmings which showed lower levels of resolved and unresolved hydrocarbons than expected based on that sample's volatile organics concentration. The Algae sample also had the highest percentage of water of all the samples from the Richmond Refinery. At the Union Oil, Rodeo site, the biosludge has a lower overall total level of hydrocarbons compared with the API separator sludge. The DAF sludge showed the lowest concentrations of total hydrocarbons on a wet weight basis, but on a dry weight basis it was comparable to the dry Biosludge. It is believed that the high total concentration of volatiles for the DAF Sludge and the Algae skimmings (Table 3-14) is due to the significantly higher water content of those two samples.

At the Chevron, El Segundo treatment facility, the IAF treated sludge had three to four times higher levels of total hydrocarbons, compared to the

PETROLEUM HYDROCARBONS IN REFINERY WASTES. CONCENTRATIONS ARE IN µg/g WET WEIGHT; NUMBERS IN PARENTHESES ARE CONCENTRATIONS IN µg/g DRY WEIGHT. TABLE 3-15.

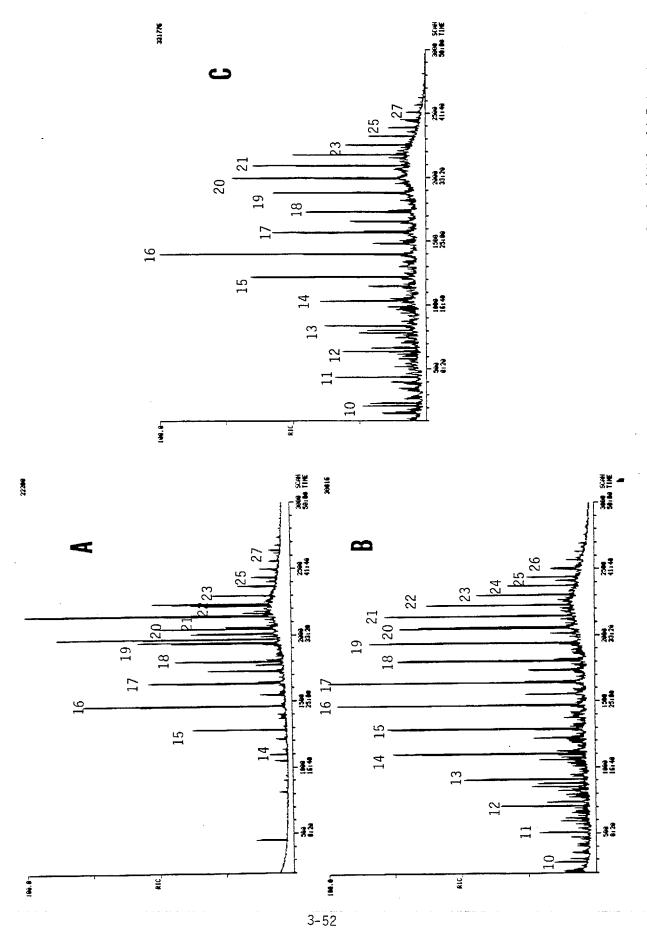
Sample Description	Conc. Total Resolved HC	Conc. Total Unresolved HC	Ratio Resolved Unresolved	Conc. Sum n-alkanes	Ratio Odd/Even alkanes	Ratio Pristane C17	Ratio Phytane C18
Union 011-Rodeo							
Biosludge	1,800 (4,500)	8,500 (21,000)	0.27	920 (2,300)	[.	0,33	0.27
API Separator Sludge	13,000 (21,000)	53,000 (87,000)	0.24	5,700 (9,300)	0.98	0.21	0.21
DAF Sludge	620 (3,900)	,3,200 (20,000)	0.19	220 (1,400)	1.0	0.19	0.21
Chevron-Richmond							
Algae Skimmings	67 (420)	480 (3,000)	0.14	5.2 (33)	0.53	7.7	2.9
Soil-HWSA	13 (14)	240 (260)	0.05	7.8 (8.6)	1.2	0.40	<u>-</u>
Soil-SP Tank Farm	1,100 (1,300)	5,400 (6,200)	0.20	633 (730)	-	7.	96.0
T-290 Tank Bottoms	75,000 (90,000)	160,000 (193,000)	0.47	20,000 (24,000)	:	12	9.1
Chevron-El Segundo							
DAF Sludge	2,300 (12,000)	13,000 (65,000)	0.17	500 (2,500)	0.47	1.7	0,33
IAF Sludge	7,400(24,000)	33,000 (110,000)	0.23	2,800 (9,000)	66.0	0.58	0.35
	- Prince	***		*		24 . 27 . 27 . 27 . 27 . 27 . 27 . 27 .	

DAF sludge; however, this was not reflected in the EPA priority pollutant volatile organics analyses for these samples as shown by the data in Table 3-14. At the time of this writing we have no explanation for this discrepancy except for the fact that the DAF sample was higher in lower molecular weight aromatics (benzene and toluene) and also contained more water.

#### Union Oil - Rodeo

Figure 3-6 presents the reconstructed ion chromatograms obtained from the base neutral extracts of the three refinery wastes collected from the Union Oil, Rodeo site. The biosludge shown in Figure 3-6A, contains intermediate levels of total resolved components with most hydrocarbons below  $nC_{14}$  not present in the sample. As noted above, the total resolved and unresolved hydrocarbons were lower in this sample compared to the API separator sludge (Figure 3-6B); however, the DAF separator sludge (Figure 3-6C) contained similar total resolved levels (on a dry weight basis) despite containing higher levels of VOA's. As was the case for the <u>volatile</u> organics analyzed from the API separator and the DAF separator, the chromatographic profiles obtained on the <u>semi-volatile</u> components appear quite similar after these two treatments.

Further examination of the chromatogram obtained on the biosludge sample (Figure 3-6A) shows that in addition to the n-alkanes present, there is a cluster of components occurring between  ${\rm nC}_{19}$  and  ${\rm nC}_{20}$ . Also there is a large single component occurring immediately after  ${\rm nC}_{21}$ , such that the n-alkane peak is really just a shoulder on the major peak following it. From research investigating petroleum degradation in marine environments, it is believed that these extraneous peaks are microbially degraded products or products generated from the microorganisms present in the samples themselves. Clearly, however, from this chromatographic profile, there are very few volatiles present, and it should be noted that the volatile components, as shown in Table 3-14, represent only 23 µg/g of sample, whereas the total intermediate molecular weight components constitute 10,300 µg/g on a wet weight basis.



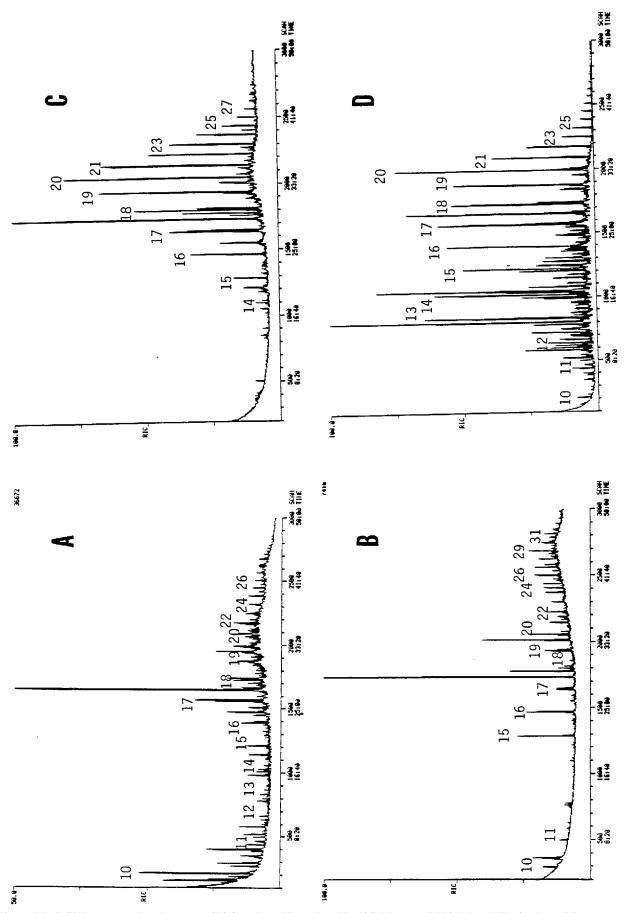
Reconstructed Ion Chromatograms Obtained From GC/MS Analysis of Base-Neutral Liquid/Liquid Extract of Sludge Samples Obtained From Union Oil, Rodeo Refinery: A) Biosludge; B) API Separator Sludge; C) DAF Sludge. Numbers above selected peaks represent number of carbon atoms in n-alkanes present in samples. FIGURE 3-6.

The chromatographic profiles of the API separator sludge and DAF sludge (Figures 3-6B and 3-6C, respectively) are qualitatively quite similar, and there is evidence of lower molecular weight alkanes and branched, isoprenoid, and aromatic components in these extractable samples down to nC $_{10}$ . Clearly, the VOA analyses of these samples shown in Figure 3-3, and the reduced data in Table 3-14 also demonstrate that these two sludge samples do contain significantly higher levels of lower molecular weight components in addition to the intermediate molecular weight hydrocarbons. It should again be noted, however, that the total mass of volatiles in these samples are quite small (160 to 180  $\mu \rm g/g$ ) compared to the total higher molecular weight components (ranging from 3,800 to 66,000  $\mu \rm g/g$  wet weight) in the extractable phase.

#### Chevron - Richmond

Figure 3-7 presents the reconstructed ion chromatograms obtained on the four sludge samples collected from the Chevron, Richmond Refinery. Figure 4-7A is the algae skimmings, and in this case, there is evidence of lower molecular weight components below scan number 200 ( $nC_{1,0}$ ) in this sample. This is correlated by the volatile organics data shown in Figure 3-4A, and by the data in Tables 3-14 and 3-15. Again, the percent water in this sample is quite high (84%). Interestingly, the intermediate and higher molecular weight hydrocarbon profile from the algae skimmings sample shows significantly reduced resolved n-alkanes, and the ratios of the isoprenoid compounds pristane and phytane to their straight chain counterparts,  $nC_{17}$  and  $nC_{18}$  (Table 3-15), suggest that the sample has undergone significant biodegradation in addition to other weathering processes. The data and chromatographic profile show quite clearly, however, that the algae skimming process yields an oil/algae sludge which contains significant levels of lower molecular weight volatile organics.

The reconstructed ion chromatograms of the soil samples from the Hazardous Waste Storage Area and the San Pablo Tank Farm are shown in Figures 3-7B and 3-7C. In line with the volatile organics analysis on the HWSA soil,



Reconstructed Ion Chromatograms Obtained From GC/MS Analysis of Base-Neutral Liquid/Liquid Extract of Samples Obtained From Chevron, Richmond Refinery: A) Algae Skimmings; B) Soil From Hazardous Waste Storage Area; C) Soil From San Pablo Tank Farm; and D) T-290 Tank Bottoms. Numbers above selected peaks represent number of carbon atoms in n-alkanes present in samples. FIGURE 3-7.

the semi-volatile organics analysis profile shown in 3-7B is relatively simple and uncomplex, and a total of only 13 micrograms/gram of resolved petroleum hydrocarbons were obtained on this dry sample. The large peak between nC and nC is the GC/MS internal standard D-10 phenanthrene.

The soil from the San Pablo Tank Farm (Figure 3-7C) does show a higher level of hydrocarbon contamination, although these materials are primarily higher molecular weight hydrocarbons above nC $_{15}$ . The total hydrocarbons in that sample were approximately 6,500 micrograms/gram of sample. This sample had a higher moisture content than the HWSA sample and exhibited intermediate levels of volatile compounds (16  $\mu g/g$ ) in line with the overall trend analysis at this site.

The final sample chromatogram, shown in Figure 3-7D is from the Tank Bottom Sludge from tank T290 at the Chevron, Richmond Refinery. This sample contained high levels of total organics (approaching 240,000 micrograms/gram of wet sample), and these included a number of intermedaite and higher molecular weight hydrocarbons from  $nC_{12}$  through  $nC_{30}$ . In addition to these nalkanes, there are also a series of unknown aliphatic or aromatic compounds eluting in a somewhat homologous fashion between  $nC_{11}$  and  $nC_{15}$ .

#### Chevron -- El Segundo

Figure 3-8 presents the reconstructed ion chromatograms obtained on the two sludge samples from the Chevron, El Segundo Refinery. Interestingly, the qualitative appearances of the chromatograms are quite similar, although the IAF sample contains three times higher levels of petroleum hydrocarbons as shown by the reduced data in Table 3-15. This quantitative (but not qualitative) difference in intermediate and higher molecular weight components presumably represents the similarity in treatment in the DAF and IAF sludge processing. In fact, the IAF sludge waste was known to contain some DAF sludge and slop oil emulsions. Interestingly, the volatile organic analyses shown in

Table 3-14 show that there is only a slight difference in volatile compositions. In this case the biggest differences are observed for benzene and toluene, where again the DAF sludge (with higher water content) is more heavily contaminated with these lower molecular weight aromatic hydrocarbons.

Both the DAF and IAF sludge samples are characterized by n-alkanes from  $nC_{10}$  through  $nC_{31}$ , and there are a number of resolved branched, cyclic and/or aromatic components in the lower molecular weight ( $nC_{10}$  through  $nC_{15}$ ) range. These are very similar to those observed in the T-290 tank bottoms sample from the Chevron, Richmond Refinery. Additional characterization of these components is currently awaiting GC/MS data reduction.

## 3.2.9 Results of EPA Priority Pollutant Semi-Volatile Organic Analyses in Refinery Wastes

The GC/MS data on the semi-volatile components were further subjected to selected ion monitoring analyses for determination of EPA priority pollutant semi-volatile organics. The results of those analyses are presented in Table 3-16. In line with the other observations, the biosludge from Union Oil, Rodeo Refinery did not contain significant amounts of any of the EPA priority pollutant semi-volatile components, whereas the API separator sludge and the DAF sludge did contain several of these components. Concentrations of the intermediate molecular weight polynuclear aromatics, including naphthalene through chrysene, were higher in the API separator sludge than in the DAF sludge, but then higher molecular weight components starting with fluorene and extending through fluoranthene and benzo(g,h,i)perylene were higher in the DAF sludge from the Union Oil, Rodeo Refinery.

The EPA priority pollutant semi-volatile organics screening of the samples from the Chevron, Richmond Refinery showed essentially no positive hits in the algae skimmings or in either soil sample. Significant levels of naphthalene, phenanthrene, fluorene, anthracene, and acenaphyene were obtained only in the tank bottom sample.

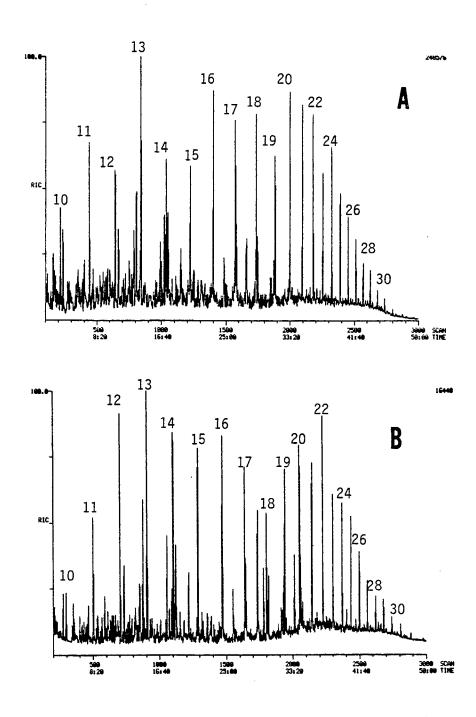


FIGURE 3-8. Reconstructed Ion Chromatograms Obtained From GC/MS Analysis of Base-Neutral Liquid/Liquid Extract of Sludge Samples Obtained From Chevron, El Segundo Refinery: A) DAF Sludge; and B) IAF Sludge. Numbers Above Selected Peaks Represent Number of Carbon Atoms in n-alkanes Present in Samples.

EPA PRIORITY POLLUTANT SEMIVOLATILE ORGANICS IN REFINERY WASTES. CONCENTRATIONS IN µg/g WET WEIGHT; NUMBERS IN PARENTHESES ARE CONCENTRATIONS IN µg/g DRY WEIGHT. TABLE 3-16.

-[Vd-Primethy]-   Lonehq		9	1.0	Q.	QN	9	S.	2		Q.	2
Phenol		Q.	0.30	QN	QN	S	QN	Q		1.9 (9.5)	2.4 (7.7)
Acenapthy) ene		¥.	Q	Q.	S	ę	QN	46 (55)		2	g.
Fluoranthene		NA	QN QN	0.14 (0.88)	S	Q.	ON.	ON		0.67	9
Benzo (g,h,i) Perylene		NA	Q	0.09	Q.	QN	QN	ON		Q	QN
Benzo (a) Pyrene		AN	2	0.42 (2.6)	S.	Q	g	£		0.32	S.
Benzo (b) Fluoranthene		NA	QN	0.37 (2.3)	QN	Q.	g	욷		0.25	Q
Anthracene		NA	QN	0.45 (2.8)	QN N	S	9	12 (14)	· -	1.3 (6.5)	Q.
Dibenzo (a,h) Anthracene		NA	S.	1.9	Q.	Q.	Q	9		9	ON
Fluorene		NA	Q.	0.56	Q	QN	S	51 (61)		3.4 (17)	QN
Сһтуѕепе		A.	150 (250)	3.1 (19)	Q.	QN	g.	Q		3.8 (19)	QN N
Benzo (a) Anthracene		NA	34 (56)	0.95 (5.9)	ND	QN	QN	QN .		1.5	ON
Pyrene		NA	24 (39)	0.80	0.03	(6.9 (8.9)	Q.	11 (13)		4.6 (23)	QN
- Риепативи- Риепативи-		NA	44 (72)	1.8	ND	ND	0.43	200 (240)		14 (70)	(190)
Naphthalene		A.	120 (200)	8.8 (55)	0.69	(°.5)	9	490 (590)		38 14 (190) (70)	82 (260) (190)
SAMPLE DESCRIPTION	Union Oll-Rodeo	Biosludge	API Separator Sludge	DAF Sludge	Chevron-Richmond Algae Skimmings	Soil-HWSA	Soil-SP Tank Farm	T-290 Tank Bottoms	Chevron-El Segundo	DAF Sludge	IAF Sludge

NA = Not Available ND = Not Detected

The DAF sludge and IAF sludge from the Chevron, El Segundo Refinery did have higher concentrations of a number of the EPA priority pollutant semi-volatile organics. As in the Union Oil DAF separator sludge sample, the DAF sludge sample from Chevron, El Segundo contained greater levels of higher molecular weight polynuclear aromatics in the pyrene through fluoranthene range. The IAF sludge from Chevron, El Segundo had higher levels of naphthalene and phenanthrene. The API separator sludge from Union showed higher levels of these two relatively lower molecular weight polynuclear aromatics compared to the DAF sludge as well. Two phenols were detected in the acid fractions of some of the refinery waste samples, and where detected, the concentrations are denoted in Table 3-16.

#### 3.2.10 PCB and Chlorinated Pesticide Analyses of Refinery Waste Samples

Electron capture detector gas chromatographic analyses of the base/ neutral extracts obtained from the refinery samples failed to show any significant matches or quantifiable levels of chlorinated pesticides or PCBs. GC/MS analyses, using selected ion monitoring techniques to screen for pesticides, failed to reveal any significant levels of the target components. Our failure to detect these materials, however, may have been confounded by the high levels of aliphatic and aromatic hydrocarbons inherent to the sludge samples.

#### 3.3 CONCLUSIONS

### 3.3.1 Comparability of Volatile Organics GC/MS Analyses and Extractable Component GC-FID Analyses

With regard to comparing results obtained by VOA GC/MS analyses and GC-FID analyses of liquid-liquid extractable components, it was noted that very similar trends in relative as well as absolute organic content were observed with both methods. That is, except for several samples with very high water content, the samples which exhibited the highest volatile organic components by the purge and trap technique also yielded the highest total resolved and unresolved complex mixtures of hydrocarbons as determined by flame ionization detector capillary gas chromatographic analyses.

# 3.3.2 <u>Heat of Combustion Analyses and Volatile/Extractable Organic Content of Sludge</u>

Heat of combustion measurements tended to parallel the overall hydrocarbon levels present in the various sludge and soil samples tested. This correlation may have been confounded, however, by residual moisture in each sample, which would inadvertently contribute to sample weight and simultaneously detract from efficient burning during the combustion analysis. Theoretically, excess water was removed from the samples prior to bomb calorimetry, but this procedure presumably only removed bulk water. That is, bulk water was removed by filtration or physical separation (decantation), and as such, emulsified water in the sludge samples could interfere with the heat of combustion measurement.

### 3.3.3 Metals vs Volatile Organic Compound Determinations in Refinery Wastes

With regard to volatile metals, the highest mercury concentrations (110 micrograms/gram) were obtained in the API separator sludge, and this material also yielded the highest overall level of "Total Concentration of Volatile Components". The Induced Air Flotation sludge showed the next highest level of mercury (17 micrograms/gram), and this sludge was also high in cadmium, chromium, copper and zinc. Lead was high compared to crustal average abundance in all of the sludge and soil samples tested as part of this program.

Most of these metals have insignificant vapor pressures in the elemental state, and as such they would not cause an air pollution problem; however, organo-metallics complexes may change their volatility such that additional analyses may be warranted in future studies to evaluate the degree of which the complexing of these metal components has occurred. The concentration of selenium was elevated in all of the samples and is one metal which does have a tendency to volatilize in environmental situations.

## 3.3.4 Implications for Compliance Monitoring and CARB's Suggested Control Measure

As a result of these analyses, it is clear that in just this one set of waste products (specifically petroleum refinery wastes), there are numerous organic and inorganic components which may contribute to volatile emissions. Assessing the potential volatile emissions from individual components in each compound class or family of potential pollutants required a significant amount of state-of-the-art instrumentation and analyses.

Complete characterization of volatile wastes in these and other potential liquid and solid waste samples using current technology, will therefore require intensive investigations and very sophisticated analytical procedures. All of these approaches are expensive, time consuming and require highly trained personnel.

The proposed gravimetric purge and trap technique, which is currently being considered as a test method for a Suggested Control Measure for controlling emissions of organic compounds from disposal sites containing volatile organic wastes is an example of an alternate analytical protocol. While this technique has suffered through many complications during its development, it does promise simplicity of operation, low cost and applicability to a wide variety of solid and liquid waste types. Additional details of SAI's investigation of this technique in collaboration with CARB personnel are given in a separate Appendix to this report.

#### 3.4 BIBLIOGRAPHY

- EPA, December 1979. Federal Register, Volume 44, Number 233. December 3, 1979.
- EPA, March 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/ 4-79-020. March 1979.

## CHAPTER 4

SURVEY OF CALIFORNIA'S HAZARDOUS WASTE INCINCERATION INDUSTRY

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# CHAPTER 4

# SURVEY OF CALIFORNIA'S HAZARDOUS WASTE INCINCERATION INDUSTRIES

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#### CHAPTER 4

# SURVEY OF CALIFORNIA'S HAZARDOUS WASTE INCINERATION INDUSTRIES

An identified objective of this study was to conduct a survey of the incinerator facilities in California that are presently active in the destruction of solid hazardous wastes. This survey was conducted in the form of a questionnaire (Appendix 4-1) that included requests for specific information on the facilities' incineration processes, origin of waste, stated purpose of the incinerator, in addition to the information requested in a similar survey conducted by CARB in 1981. This chapter of the SAI Toxic Waste study for CARB presents:

- a summary of the rules and regulations governing the incineration of hazardous waste; and
- summaries of the responses to the questionnaires of the surveys conducted in 1983 and 1981.

#### 4.1 REGULATIONS PERTAINING TO INCINERATION OF HAZARDOUS WASTE

### 4.1.1 Federal Regulations

The bases for all Federal regulations governing the operation of waste incinerators are the Clean Air Act and the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976 (RCRA). The specific Federal regulations which prescribe the system of permits and standards for regulating hazardous waste management facilities are in Title 40, Parts 260-267, 270, 271, and 124 of the code of Federal Regulations (40 CFR), which specify the mechanics of controlling hazardous wastes.

To facilitate the review by EPA of the applications for permits to operate hazardous waste facilities, the permit system has been divided into

two parts, Part A and Part B. The Part A application (40 CFR 270.13) requires information on location, description of the process to be used to dispose of the hazardous material, and a specification of the type and quantity of waste to be processed; the Part B application (40 CFR 270.14-270.21) requires that detailed information be submitted including chemical and physical analyses of the wastes to be processed, safety precautions and procedures, training programs, liability coverage, financial status, description of the topographical and geological site of the HWM facility, and the results of a trial burn.

RCRA also allowed for an "interim status": if an HWM facility was in existence on or before November 19, 1981, and if it submitted a RCRA Part A application, the "interim status" would allow it to legally conduct operations prior to receipt of a final permit after submission of a Part B application. During this period of interim status, however, the facility must comply with interim status standards as specified in 40 CFR 265, and when requested to do so by EPA or an authorized state, prepare a RCRA Part B application to demonstrate compliance with the standards for HWM facilities set forth in 40 CFR 264.

Under section 3006(b) of RCRA, provision is made for the eventual authorization of the individual States to administer and enforce their own hazardous waste program, provided that program is consistent with the definitions and standards set forth in 40 CFR.

Volume 48, No. 65 (April 4, 1983) of the Federal Register describes changes that the U.S. EPA is currently proposing to make in 40 CFR, including proposed changes in the definition of incinerators (Section V). These changes are intended to extend 40 CFR 264 regulation to include all facilities involved in the thermal destruction of hazardous wastes. For example, boilers have been exempt from 40 CFR 264 regulations because their primary purpose is to recover heat from the combustion process and not the thermal destruction of hazardous waste. This loophole in the permit and standards system for hazardous waste incineration has been exploited to the maximum, an estimate having

been made that 20 million metric tons of hazardous waste are currently being burned in boilers (H.R Rep. no. 97-950). To remedy this particular situation the EPA has proposed 35% as a standard for the minimum amount of energy recovered from the combustion process. The net result of the adoption of this standard will be to increase the number of facilities regulated under 40 CFR 264 and ultimately improved control over what and how much is emitted.

#### 4 1.2 State Regulations

In California, the State Health Department regulates Hazardous Waste Management (HWM) facilities through a system of permits and approved operation plans as specified in Article 4 of Title 22 of the California Administrative Code. The "operation plan" that must accompany an application for a hazardous waste facility must conform to Section 66376 of Title 22 and is essentially a more detailed "standard" for HWM facilities than is set forth by the Federal Regulation 40 CFR 264 (referred to in RCRA Permit B applications). Articles 9 and 10 of Title 22 contain listings of the chemical and common names of materials considered to be hazardous waste. The State Department of Health also administers the hazardous waste manifest system and the temporary (up to 12 months) Extremely Hazardous Waste Disposal Permits. Section 66360 of Title 22 describes the conditions under which the State Department of Health will delegate enforcement authority to "a local public officer".

#### 4 1.3 Local Regulations

The regulation of hazardous waste incinerators on the local level is accomplished through each of the state's 44 Air Pollution Control Districts. Under the existing local permit programs in California, any new or modified source which may cause an issuance of air contaminants is subject to review and must obtain a permit to operate from the applicable District.

#### 4.2 1983 INCINERATION SURVEY DESCRIPTION

A list of facililties to be included in SAI's 1983 Survey of Hazardous Waste Incinerators in California was compiled by:

- obtaining a list of incinerator facilities in California that had notified the EPA that they processed hazardous waste, as is required under Section 3010 of RCRA and that had a Part A application on file; and by
- contacting each of the facilities listed by CARB to determine if it was still in operation and to identify which person at that facility would have the expertise necessary to complete the questionnaire;

The questionnaire (Appendix 4-1) used in the 1983 survey was designed to:

- collect updated responses to the questions asked in the 1981 CARB survey;
- obtain information on the processes that produce the waste being incinerated (Question 5);
- determine the number of hazardous waste incinerator facilities that classify the purpose as including the recovery of heat to generate power (Question 8); and
- obtain information on the type of substances that are present in the emissions of these facilities (Questions 10 and 12).

#### 4.3 DISCUSSION

## 4.3.1 Incinerator Facility Descriptions

The initial list of RCRA notifiers and Part A applicants operating hazardous waste incinerators in California contained 22 facilities. Of these 22, only 19 were found to be in operation as of January 1983, and of these 19, 11 facilities responded to the SAI 1983 questionnaire. The remaining eight facilities are either fume incinerators or they have discontinued their

incineration activities. Tables 4-1 and 4-2 summarize the 11 respondents, identifying each with sequential code number (1 through 14). Table 4-3 contains data from the 1981 CARB survey.

Three of the 11 facilities (1, 2, 11) indicated that their waste streams do not contain RCRA listed hazardous chemicals; this can be explained by:

- the description of their waste streams were not complete;
- the facilities filed a Part A application because they did not understand which waste materials needed to be regulated;
- the facilities are regulated under the California hazardous waste code and felt they should also be identified under the RCRA system.

Facility 9 is an example of a plant producing pathological or infectious waste products which will be regulated by the State in the future under the system described in Section 4.1.2. The remaining waste streams are predominantly process waste from inorganic and organic synthetic chemicals industries; one incinerator is a sulfuric acid regeneration facility (14). Table 4-2 includes a comparison of waste type to known air emission products from the incineration process.

Each facility is operating under a permit from its local air pollution control board. As expected, the local permits have limitations of NOx, SOx, air suspended particulate matter and odor, and several have monitoring and quality assurance requirements for operating conditions.

TABLE 4-1. CALIFORNIA INCINERATOR FACILITIES SUMMARY - 1983 SURVEY (Plant numbers indicated below are same as in 1981 survey)

Plants	No. of Waste Streams	Annual Amount of Waste Pro- cessed	Reason for Incinerator Installation	Purpose of Incinerator	Purpose of Permit from Air Pollution Central Districts
*Plant l	1	600 tons	Air Pollution control	To control ris- ing odor from Polyester production	Regulation
*Plant 2	1	250 tons	APCD Require- ment odor & organic emis- sion control	Condensed organic vapors reclaimed as energy source	Odor and emission control APCD Requirement
Plant 3	8	6,500,000 gals., 11 months	Incinerate waste from manufacturing process	To incinerate waste	Regulates air pollutants
Plant 5	1	24,800 lbs.	Security & economy	To incinerate waste	Control visible emissions and particulate matter emissions
Plant 8	2	260 tons	Production fume control	Fume control a waste heat boiler & an aqueous waste system were added	Restrict emission of NO <sub>x</sub> , SO <sub>x</sub> particulate
Plant 9	2	50 tons	Incinerate pathological material and woodshavings.	Incinerate waste	Revenue and quality assurance
Plant 10	1	457,998 gals.	Disposal of fumes	Steam is also generated for plant proces- sing	Air pollution control system
Plant 11	2	600 tons	Odor control and distruc- tion of acidic aqueous waste stream	To incinerate odorous air emissions	Regulations require permits to determine compliance and monitor emissions
Plant 12	1	7,400 tons	Improvement of solid wastes disposal operation, energy conservation, method and destruction of sensitive material generated by govt. contracts	To utilize the available energy in solid waste to reduce electrical power required for environmental heating & cooling 2 plant buildings	Restrict emission of NO <sub>X</sub> , SO <sub>X</sub> particulate
Plant 13	2	119 tons	To dispose of waste from pro- prietary chemi- cal Mftr. decrease disposal cost and receiving of useful energy	To incinerate waste for steam generation	Regulations require a permit to operate any equipment which may cause, reduce or control air cor amination
Plant 14	2	51,900 tons	To regenerate spent sul-furic acid from local refineries & soap Mftr.	Regenerate spent H <sub>2</sub> SO <sub>4</sub> to manuf. virgin soap	SO <sub>2</sub> abatement

<sup>\*</sup>These incinerators are not considered to be hazardous waste incinerators by DOHS.

TABLE 4 -2. CALIFORNIA INCINERATOR FACILITIES DATA - 1983 SURVEY

Plants	Type of Incinerator	Age (years)	1	Temperature Kange ( <sup>O</sup> F)	Dwell Time * (Seconds)	Origin of Waste	Waste Type (s)	% of Waste (Composition by wt.)	By-Products in Incinerator Exhaust
Plant 1	Thermal Oxidizer	∞	3.5x10 <sup>6</sup>	1450	m,	Polyester Resin Mftr.	H <sub>2</sub> 0 Propiendaldehyde Cyclic glycol Ether	90 5	NO <sub>X,</sub> CO Hydrocarbons
Plant 2	Forced Draft After Burner	6	5.2×10 <sup>6</sup>	1400-1600	9.	Alkyd & Polyester Resins, vapors	Hydrocarbon	ω	CO <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub> , recovering heat via steam boiler
Plant 3	Thermal Oxidizer W/Liquid Injection	16	158 ×10 <sup>6</sup>	1800-1900	<2.0	Agricultural Chemicals Manufacturing	Pesticides Other Organics Sulfides	7 69 24	None >99.99% Destruction Efficiency
Plant 5	Thermal-Tech	2.5	1.0×10 <sup>6</sup>	1200-2200	N/A	Waste generated from exceeded Shelf life, breakage, item deletions	Plastic Paper-misc. Data cards Brown paper/Card- board Drugs/Narcotics	30 30 10 40	Particulates, SO <sub>x</sub> , CO, Hydrocarbons, NO <sub>x</sub> , Aldehydes
Plant 8	Thermal Oxidizer	6	8.0×10 <sup>6</sup>	1460(norm.) 1200-1550	e.	During heating phase of syn- thetic resin production, vapors are generated by organic solvents	H <sub>2</sub> 0. Butyl Alcohol MEK Butyl Cellosolve MIBR	92.0% 2.5% 1.2% 1.1% 1.0%	NOX,COX
Plant 9**	S-3 2 compartment O-1 waste	11	Not known	1700-1900	۴.	Woodshavings from animal bedding.	Wood shavings plastic	95 5	Wood ash
	S-4 2 compartment pathological	12	Not known	1800-2000	<i>ب</i>	Pathological from animal research	Animal remains	100	calcined bone

\*Dwell time = residence time of waste in burn cycle.
\*\*Plant is not an hazardous waste incinerator.

TABLE 42. CALIFORNIA INCINERATOR FACILITIES DATA - 1983 SURVEY (Continued)

							contri (contringen)	(n	
Plants	Type of Incinerator	Age (years)	Rated Capacity (BTU / hr)	Temperature Range ( <sup>O</sup> F)	Dwell Time * (Seconds)	Origin of Waste	Waste Type(s)	% of Waste (Composition by wt.)	By Products in Incinerator Exhaust
Plant 10	Oxidizer & Boiler	£	4.0x10 <sup>6</sup>	1400	5.	Esterification rx≯H <sub>2</sub> 0	H <sub>2</sub> 0 Hydrocarbons	90-93 7-10	Waste heat, $C0_2$ , $H_20$
Plant 11	Thermal Oxidizer	٧	2.5×10 <sup>6</sup>	1700 (typical) 1400-1800	.45	Polyester Resin manuf.	N <sub>2</sub> /H <sub>2</sub> O Hydrocarbons/ organics	90 10	со2, н20
Plant 12 8-4	Two Stage combustion	25	16.0x10 <sup>6</sup>	1400-1750	3600	paper, cardboard plastic pkg. blueprints, magnetic tape, carbon paper, cafeteria wastes, resulting from light industrial manuf.	Cellulose Plastic and other organics Silica and Metals Moisture Sulfur, Chlorides, fluorides	87.9 5 2 1	Gaseous oxides of S,N <sub>2</sub> ,C, H <sub>2</sub> 0 uncondensed paper & plastic decomposition products and alkaline silicate particulates
Plant 13	20-F Custom Design	=	1.2x10 <sup>6</sup>	1400-1800	2.3	Gaseous and liquid wastes from proprietary chemical produc- tion	Toluene Proprietary chemicals	N/A N/A	H <sub>2</sub> 0, с0 <sub>2</sub>
	F-62, 64, 68 CO Boiler	17	54.0×10 <sup>6</sup>	1700-2100	.6-2.0	DAF & Bio Sludges of Oxazolidone is mixed with sludges for burning	H <sub>2</sub> 0 0il Solids Oxazolidone Sulfolane Dilsopropano-	95 2-3 92 5	NO <sub>x</sub> , SO <sub>2</sub> , H <sub>2</sub> O, CO <sub>2</sub> and Particulate matter
Plant 14	l-Horizontal liquid gas/ injection	4]	12.2x10 <sup>6</sup>	1800	8.17	Variety of oil and soap	H2504 H20 G5C8 Sulfates	88 5 3	Hydrated oxidized sulfurs, NO <sub>x</sub> , CO <sub>2</sub> , H <sub>2</sub> O
	2-Horizontal liquid gas/ injection	39	12.2x10 <sup>6</sup>	1800	7.84	Refining processes	H <sub>2</sub> SO <sub>4</sub>	78	
*Dwell Tir	*Dwell Time = Residence time of waste in burn cycle.	of wast	e in burn cycle.	-			8,9	•	

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TABLE 4-3. CALIFORNIA INCINERATION FACILITIES DATA - 1981 From California Air Resources Board Survey

	Type of Incinerator	Age (years)	Rated * Capacity (BTU/Hr)	Temperature Range ( <sup>O</sup> F)	Dwell** Time (Sec.)	Waste Type(s)	%of Waste	Waste Stream #	Annual Amount of Waste (total)
Plant 1	Thermal Oxidizer	7-8	3.5×10 <sup>6</sup>	1400-1450	unknown	H20 Propianaldehyde Cyclic Glycol Ether	90	-	600 tons
Plant 2	Forced Draft Fume	7	5.2 x106	1300-1500	9.	Air Hydrocarbon	75 25	_	251 tons
Plant 3	Thermal Oxidizer	14	158 x 10 <sup>6</sup>	1800-1900	1.6	VOC H2O/process intermediate	96	4	3,400,000 gals.
4-9	-			· · · · · · · · · · · · · · · · · · ·		H2O Pesticide VOC	98 .25		2,400,000 gals.
						H20 Pesticides & intermediates NH3 NH4+ Cmpds. Na Salts Methyl Sulfonic acid	70 3 22 22 2		9,700,000 gals.
	:					VOC Pesticides & intermediates Organic polysulfides Dimethyl Sulfides	43 17 20 20		967,000 gals.
Plant 4	Thermal Oxidizer	11	8.0 ×10 <sup>6</sup>	1200-1400	.3	Aromatic HC Aliphatic HC Organics	50 20 20	_	9,784 lbs.
Plant 5	Hospital Waste Incinerator	-	0.1-1.1x10 <sup>6</sup>	1200-2200	N/A	Drugs/Narcotics Paper Plastic	80 15 5	_	24,824 lbs.

\*This is a rated capacity of the unit and does not reflect the amount of waste incinerated, \*\*Dwell time = residence time of waste in burn cycle.

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(continued) CALIFORNIA INCINERATION FACILITIES DATA - 1981 CARB SURVEY TABLE 4-3.

	Type of Incinerator	Age (years)	Age Rated * (years) Capacity (BTU/Hr)	Temperature Range (oF)	Dwell** Time (Sec.)	Waste Type(s)	% of Waste	Waste Stream #	Annual Amount of Waste (total)
Plant 6	Direct Flame	6	12×106	800-1600	9.	Vinyl aliphates Methylamine Vinyl aromatics Methylal Others	38 30 15 13		87,600 lbs.
Plant 7	Fire Tube Package	18	1.6x10 <sup>6</sup>	1500-2500	z.	Fuel MEK	Reclaimed		N/A
O Plant 8	Thermal Oxidizer	8	8×10 <sup>6</sup>	1200-1500	m.	H20 Butyl alcohol MEK Butyl cello solve MIBK Others	92.0 2.5 2.2 1.2 1.1	2	260 tons
Plant 9	2 compartment 01 waste	17	Not known	1700-1900	e,	Wood shavings Plastic	95 5	2	50 tons
	2 compartment pathological	12	Not known	1800-2000	£.	Animal remains	100		1,800 lbs.

\*This is a rated capacity of the unit and does not reflect the amount of waste incinerated. \*\*Dwell time = residence time of waste in burn cycle.

The ages of 14 incinerators (among the 11 facilities) vary widely, from less than a year to over 40 years. Some are an integral part of the processing system, while others were installed to control odors and recover heat to supply energy back to the facility. Rated capacities (BTU/hr) were found to range from 1 million to 54 million with the average being 11.3 million. This compares with an average rated capacity of 7.9 million BTU/hr obtained from the CARB 1981 survey (Table 5-3).

Operational temperatures varied from 1400°F to 1900°F, with the average being 1600°F. The dwell time (seconds; residence—time of waste material in the burn cycle) ranged from <0.2 to 8.17, except for one two-stage combustion process with a dwell time of 3600 sec (1 hour). Excluding the 2-stage combustor, the average dwell time is 2 seconds; the standard deviation is 2.9 seconds.

At least three of the plants (9, 13, 14) from the 1983 survey dealt with two waste streams using two incinerators, while the other seven operate one to handle a single dominant waste stream. One plant has one incinerator which handles eight waste streams. The respondents to the 1983 survey commonly listed the following as emissions from their incineration processes: NOx; SOx, COx, hydrocarbons and particulate matter.

#### 4.3.2 Incinerated Waste Quantitation

In order to quantify the total and average hazardous waste amounts processed by these facilities responding in the 1983 survey, several assumptions were made. Facility 14 was disregarded because of its function as an acid regeneration facility as opposed to being a waste destruction facility. Then, for the remaining 10 facilities, the annual total waste stream in pounds was multiplied by the percentage of that waste stream that was either specifically identified as being hazardous, or was identified in a generic sense that could be reasonably be assumed to include hazardous waste. Approximately 50,000 tons of total hazardous waste are being incinerated according to respondents to the 1983 survey, compared to 28,800 tons reported in the 1981 CARB survey.

#### 4.4 BIBLIOGRAPHY

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## APPENDIX 4-1

SAI 1983 Incineration Industry Questionnaire

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# INCINERATION FACILITIES OPERATIONAL QUESTIONNAIRE

Façi	lities Identification	'		
	Name of Company:		<del></del>	
•	Plant Name:			
	Plant Address:			
	Contact Person/Title	:		
	Mailing Address:			
	Phone Number:			
Back	ground Information			
1)	When were incinerati	ion capabilities e	established at th	is plant address?
2)	How many incineration	on units are curre	ently in operation	n?
3)	Description of Incin	merator(s):		
	Unit #			<del> </del>
	Туре			
	Brand Name			
	Model #			
	Age (Years)			
	Rated Capacity (Btu/Hour)			
	Fuel Type			
	Heating Value (Btu per 1b; gallon or CF)			
	Fuel Consumption (CFM, GPM, or lb/Hour)			
	Waste Consumption (CFM, GPM, or 1b/Hour)			
	Temperature Range in Incinerator (°F)			

Combustion Excess Air (%)	
Oxygen Level in Exhaust Gas (%)	
Dwell Time (Seconds)	
Description of Waste Stream:	
Waste Stream No.	
Chemical Make Up (Please indicate	
Unit in Which Wastes is Incinerated	
SIC Code of Process That Generated the Waste	
Liquid Waste GPM	
Gaseous Waste CFM	
Solid Waste Lb/Hr	
Annual Rate of Waste (Total)	
Description of Process:	

5)	Describe the origin of the wastes that are being incinerated, or the process description that produces the waste:
6)	What was the initial reason for installation of the incinerator(s)?
7)	Are there future plans for expansion of incineration capabity at this plant or other plants owned by this company?
8)	a. Is heat recovery currently used or proposed?
	b. Is the sole purpose of the incineration equipment listed above to incinerate wastes? If not, describe the purpose:
	c. Are energy penalties being accessed to your facility from current incineration activites?
9)	What are the estimated annual costs for waste disposal associated with the incinerators?
10)	Does your incinerator(s) require an operating permit from local Air Pollution Control Districts?
	If yes, what is the purpose?
11)	What type of incinerator exhaust monitoring devices are currently in use?

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What were the incinerator(s)	initial cost	s (i.e., h	ardware and	installatio	on costs)	for
					<del>\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\</del>	